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TEMPERATURE

Its Measurement and Control In Science and Industry

Papers presented at a Symposium held in
New York City, November, 1939

under the auspices of the

AMERICAN INSTITUTE OF PHYSICS

with the cooperation of

NATIONAL BUREAU OF STANDARDS
NATIONAL RESEARCH COUNCIL

and officers and committees of

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AMERICAN CHEMICAL SOCIETY
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REINHOLD PUBLISHING CORPORATION
330 WEST FORTY-SECOND STREET, NEW YORK, U. S. A.
1941

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Second printing, 1947

Printed in the United States of America by
THE GUINN CO.

Foreword

This book is the record of a "Symposium on Temperature—Its Measurement and Control in Science and Industry," held in New York, November 2, 3 and 4, 1939, under the auspices of the American Institute of Physics. In organizing a Symposium on this subject the Institute commemorated the 20th anniversary of a well-known "Symposium on Pyrometry," the published papers of which are still valuable as references. At that earlier time the subject was well understood and its importance fully appreciated only in the high-temperature industries, such as steel and ceramics, and in a few laboratories. Since then its importance has grown remarkably. An International Temperature Scale has been established, many universities have placed more emphasis in their curricula upon training in the measurement of temperature, heat transfer, etc., new industries dependent on temperature measurement and control have sprung up, measuring and controlling instruments of greatly improved design and accuracy have become available, and engineering societies have established standing committees especially concerned with the subject. In fact progress has been so marked and diverse that the usefulness of the Symposium here recorded is self-evident.

In view of these developments the Institute planned the Symposium with the following purposes in view: (1) coördination of the treatment of the subject of temperature in the several branches of science and engineering, (2) review of fundamental principles and a recapitulation of recent progress, (3) accumulation of contributions for a comprehensive text to be published after the Symposium, (4) emphasis on the importance of temperature as a branch of physics, (5) improvement of technical curricula through making the latest information available.

In addition to the foregoing specific purposes, more general motives also actuated the Institute in holding the Symposium—motives intimately related to the general aims of the Institute. The American Institute of Physics was founded by five national societies composing its membership organization:

The American Physical Society
The Acoustical Society of America
The Optical Society of America
The Society of Rheology
The American Association of Physics Teachers

The Institute is the coöperative agency of these societies and expresses the underlying unity of physics throughout its broad scope of applications. It is a part of the Institute's purpose to call attention to the industrial importance of physics and to give service to and obtain recognition for those fields of physics which have developed into important branches of science and technology. To this end the Institute has organized several special conferences and symposia in such fields as metallurgy, textile manufacture, biophysics and automotive engineering. The concept of temperature and, in general, the principles of measuring and controlling temperature lie within the realm of physics. They provide an example of the underlying unity already referred to, because the principles are the same no matter in what direction they are applied. Needless to say, the number of technical fields in which temperature is important is very large. Indeed it is hard to name a field in which temperature plays no role.

It is immediately obvious that, while it was appropriate for the American Institute of Physics to initiate arrangements for a symposium on temperature, the value of the symposium would accrue to chemists, biologists, geologists, engineers, physicians and those bearing many other professional designations. Moreover, it was largely among these same groups that the best authorities were to be found on the subjects appropriate for discussion. The Institute accordingly sought wide coöperation in the arrangement of the program. The Symposium could hardly have been as successful as it was if a large number of organizations officially or informally through officers and committees had not coöperated in the task of program construction. The Institute hopes that they share its own pride in the result, and takes this opportunity of placing on record its very great indebtedness to the coöperation received through the following:

National Bureau of Standards
National Research Council
American Ceramic Society
American Chemical Society
American Institute of Mining and Metallurgical Engineers
American Society of Mechanical Engineers
American Society for Metals
American Society of Heating and Ventilating Engineers
American Society of Refrigerating Engineers
American Society for Testing Materials
American Standards Association
American Welding Society
Society of Automotive Engineers
American Foundrymen's Association

The heaviest single burden fell on the staff of the National Bureau of Standards. The Bureau was well represented on the program, largely through the coöperation of Dr. H. T. Wensel; and, indeed, the nature of the Bureau's work is such that no very valuable program could have omitted such a representation. It is particularly appropriate to acknowledge indebtedness to Dr. Lyman J. Briggs, Director, and to many members of the Bureau staff.

The National Research Council, in its role as coördinating agency of science in the United States, contributed greatly through its coöperation. Certain expenses were met with the help of a grant from the Council.

In common with other enterprises of a like nature, the arrangement of the Symposium required the expenditure of a great deal of time and effort by the members of several committees, which are listed on pages v and vi. For all who are profiting from the Symposium, the American Institute of Physics acknowledges in this place the very great debt owed to these men. The original design of the Symposium was laid out by the Advisory Committee. The details of preparation fell particularly on the Symposium Committee. In both respects these committees depended on the initial inspiration and subsequent enthusiasm of Mr. C. O. Fairchild of the C. J. Tagliabue Manufacturing Company. The members of this committee served as chairmen of subcommittees and were responsible each for an important field of the general subject.

Since the holding of the Symposium, all the papers have undergone a careful process of editing under the supervision of a Publication Committee composed of the following:

C. O. Fairchild J. D. Hardy R. B. Sosman H. T. Wensel

It is under the direction of this last committee that this book now appears as a permanent record.

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Chairman, Governing Board
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Introduction

The Symposium was held November 2, 3, and 4, 1939, in the Hotel Pennsylvania, New York, where more than 800 individuals, of whom 612 were officially registered, attended one or another of twenty sessions, which took place in concurrent groups. The program included the presentation and informal discussion of approximately 125 papers arranged in the sessions to avoid conflicting interests as far as possible.

Dr. John T. Tate, Chairman of the Governing Board of the American Institute of Physics, formally opened the Symposium at a General Session and addressed a few remarks of welcome to those in attendance. This session was then turned over to Dr. Lyman J. Briggs, Director of the National Bureau of Standards, who presided. After emphasizing the great value of the Symposium to science and industry, Dr. Briggs called in order for five papers of general and markedly contrasting interests, which are listed herewith.

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In accordance with previous plans the Symposium papers, with the discussions, have been rearranged for publication in the thirteen chapters following, together with twenty-five tables of generally useful data, a Glossary of technical terms, and complete indexes. The arrangement has been designed to make the book most convenient both for reference and study, but few papers being found in arbitrarily chosen sequence. Bibliographies are to be found at the ends of individual papers, in many cases being rather extensive. To a large extent many topics have been brought up to date, and with a few faults of omission, the whole presents a fairly comprehensive picture of the present state of knowledge of the fundamentals of the broad subject.

No attempt was made to edit the papers to a uniformity of language or even of the use of words having special meaning. The attention of all of the authors was called to the desirability of a uniform use of mathematical symbols,* but no concerted attempt was made to alter manuscripts in this respect, nor did it appear practicable to include a table of symbols with the glossary of terms.

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* See page 342.

Chapter 1

Temperature and Temperature Scales

Temperature*

H. T. Wensel

Chief of Pyrometry Section, National Bureau of Standards,
Washington, D. C.

I. Heat and Temperature

Our fundamental concept of temperature is obtained from the sensation of warmth or cold which we experience upon touching any object. Such expressions as "ice-cold," "cool," "tepid," "lukewarm," "warm," "hot," "sizzling," "red-hot," etc. indicate that our qualitative appreciation of temperature precedes our use of numerics to characterize it. Our experience further tells us that when two similar bodies at different temperatures are placed in thermal communication (and cut off from such communication with all other bodies) the hot body becomes colder and the cold body becomes hotter until the two reach a thermal state or temperature which, judged by our senses, is the same.

On the other hand, our concept of what takes place during this equalization of temperature is obtained only after considerable inductive reasoning to generalize a great mass of quantitative data.

It was in the 1790's that the American physicist, Benjamin Thompson (Count Rumford) made his quantitative measurements of heat while boring the King of Bavaria's cannon. However, the generalization of our concept of heat, which we find in Helmholtz's paper on the conservation of energy, did not appear until 1847. Our concept of heat, as an exact physical term, is defined as "energy that is transferred from one body to another by a thermal process," where, by a thermal process, is meant radiation, conduction, and/or convection.

Our observation then, plus our concept of heat exchange as an energy transfer, enables us to say that in the equalization of temperature, heat passes from the hotter to the colder body. In seeking for a definition of temperature, therefore, we find it difficult to improve on the one given by Maxwell, which is that "The temperature of a body is its thermal state considered with reference to its ability to communicate heat to other bodies."

Of two bodies having different temperatures, the one which communicates heat to the other is said to be at the higher temperature, and in devising temperature scales (*i.e.*, in assigning numbers to definite thermal states) its temperature is customarily, though not necessarily, assigned the greater number. In that connection it may be of interest to mention the fact that the first scale which divided the interval from the freezing point to the boiling point of water into 100 degrees (*i.e.*, the first centigrade scale) was one devised by Celsius on which the freezing point of water was numbered 100 and the boiling point 0.

Suppose we have a body *A* which can communicate heat to a body *B*, *i.e.*, *A* is at a higher temperature than *B*. Experience shows that if a third body, a thermometer, is placed in intimate thermal contact with *B* (the colder) and allowed to remain there until all heat transfer between them has ceased, the thermometer, when now placed in contact with *A* will, *in general,* receive heat from the latter. Conversely, if the quantity of heat which a body *A* can communicate to a particular thermometer is greater than that which *B* can communicate to that same thermometer, then *A* will *in general* be able to communicate heat to *B*. When this is not the case certain difficulties must be faced.

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* The treatment presented here is very similar in parts to that given in the article on "Temperature" by Joseph S. Ames in the Pyrometry Symposium of 1919 published by the A.I.M.M.E. In addition, the author has made use of lecture notes supplied by Professor Ames to his students during the early 1920's.

If a piece of platinum is placed in the stream of illuminating gas from an unlighted Bunsen burner, the platinum will get hot even though it and the gas were initially at the same temperature. The platinum will catalyze the combination of the gas with oxygen even at room temperatures. In fact gas lighters have been made using this principle. The transfer of energy from the cold gas to the platinum is not a simple thermal process but involves a different kind of process, a chemical reaction. A bare platinum thermocouple or a bare platinum resistance thermometer, therefore, cannot indicate the temperature of a gas or of a flame. Questions of how we measure temperatures in a flame, in an electric discharge, etc., are discussed by other contributors to the Temperature Symposium. The present discussion is limited to cases in which the bodies to which temperature numbers are to be assigned are free of all electrical and chemical changes and in which the introduction of the temperature measuring device does not give rise to such changes.

II. Temperature Scales

The process of assigning numbers to temperatures is analogous to the process of naming streets and numbering houses so that the location of any particular building may be unambiguously specified. Since the number of buildings in any city is finite, we are not restricted to numbers for designating buildings. Such designations as "Flatiron Building," "Madison Square Garden," and "Cotton Club" are perfectly definite. A similar scheme will serve for some but not for all temperatures. There are a number of thermal states or temperatures which may be recognized and uniquely characterized by definite phenomena which take place at these temperatures. The most important of these temperatures (so-called "fixed points") are the melting and boiling points of pure substances at a specified pressure. But inasmuch as there is an infinity of thermal states or temperatures between these fixed points, the first requirement for the general measurement and specification of temperatures is a scale of numbers.

To assign numbers to temperatures we select some suitable substance, then some property of this selected thermometric substance, and finally some function relating the temperature to this property. The temperature scale so defined will be only one of a large number of possible ones. It will depend in general on all three selections—the thermometric substance, the property, and the function. The property may be the length of a definite piece of metal, the volume of a definite quantity of mercury held in a definite solid, the pressure exerted by a definite mass of a definite gas at a definite volume, the electrical resistance of a definite piece of wire, etc. Any such thermometric device ceases to be useful for defining a scale if its thermometric property ceases to change as heat is abstracted from it or if it undergoes such changes owing to use that, when it returns to its original thermal state after such use, it gives a reading differing significantly from the original one.

Suppose we select as basic fixed points the melting point of ice (ice point) and the boiling point of water (steam point), each at a pressure of one standard atmosphere (1,013,250 dynes/cm^2 = 1.01325 bars), and assign to them the numbers 0 and 100, respectively. We can define a scale by making equal increments on the scale correspond to equal increases in the length of a tungsten rod. Thus 50° would be the temperature at which the length of the rod is halfway between its length at 0° and its length at 100° or in general

$$t = 0^\circ + \frac{L_t - L_0}{(L_{100} - L_0)/100}.$$

Are the degree intervals on this scale equal? Experience shows that the length of a rod of *copper* will be halfway between its length at 0° and its length at 100° at a temperature which on our tungsten rod expansion centigrade scale is 54°. If we divide up the interval in proportion to the change in electrical resistance, the *resistance* scale based on copper will agree with the *expansion* scale based on tungsten to within a very small fraction of a degree. The resistance scale based on tungsten agrees with none of the other three. Which property divides the scale equally? Which material? Aside from this, the linear function chosen, even though the simplest choice, is entirely arbitrary.

This illustrates a fundamental property of temperature which is often lost sight of: namely, that temperature is an intensive and not an extensive quantity. There can be no unit temperature interval, which can be successively applied to measure any other temperature interval as can be done in the measurement of such a quantity as length. The size of a degree on one part of a scale, *no matter how defined,* can bear no relation to the size of a degree on any other part of the scale.

The various temperature scales that have been and still are in use differ in the thermometric substance employed, the thermometric property utilized, or in the function selected to represent the relation between the property and the temperature. Scales which differ in either of the first two features are fundamentally different. The difference between two scales, which differ only in the function chosen, is only superficial, because conversion from one scale to the other is merely a matter of calculation and can be made with mathematical precision.* Changing the numbers assigned to the fixed points makes no real change in the *character* of the scale and is perhaps the simplest way that the interpolation function can be changed. Thus we have the centigrade, Fahrenheit, and Reaumur scales, on which the *fundamental interval* from the ice point to the steam point is divided, respectively, into 100, 180, and 80 intervals of 1° each. In the original forms, the ice point was designated, respectively, 0 °C, 32 °F, and 0 °R, and conversion from one scale to the other is made as follows:

$$n\ {}^\circ\mathrm{C} = (0.8n)\ {}^\circ\mathrm{R} = (1.8n + 32)\ {}^\circ\mathrm{F}. \tag{1}$$

It is sometimes convenient to increase all the numbers for temperatures on these scales by a suitable, constant amount, in order that the lower limit of temperature ("absolute zero") shall be designated as 0°. The amount by which a scale should be increased to accomplish this result depends upon the thermometric property and cannot be known exactly, since it must be experimentally determined. However, since the amount by which a scale has been shifted in any given case is known, this shift can be taken care of also with mathematical precision.

On the other hand, two scales which employ either different thermometric substances or different thermometric properties differ by an amount which can be determined only by experiment. If the same basic fixed points are employed the scales will necessarily agree at these points, but not at other points. Two scales, both based on the apparent expansion of mercury in glass, will differ unless the kind of glass used is the same. The scale based on the change in pressure, at constant volume, of a definite mass of nitrogen differs from the scale based on the change in volume of the same gas at constant pressure. The constant-volume nitrogen scale with initial pressure (at the ice point) of 500 mm of mercury differs from the constant-volume nitrogen scale with 1000 mm initial pressure.

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* Two scales which are based upon the same thermometric property and the same thermometric substance but upon different fixed points are not considered here. In this case the difference is fundamental only in the sense that conversion from one scale to the other can be made only on the basis of experimental data.

Mercury-in-glass thermometry is limited to the range from the freezing point of mercury to the softening point of glass, while gas thermometry becomes difficult at very low temperatures and is limited at the high temperature end by difficulties of keeping the gas confined. A scale based on electrical resistance likewise becomes useless at "superconducting" temperatures, and at high temperatures the resistance will change at constant temperature due to permanent changes occurring in the metal even when still far removed from the melting point.

The ideal temperature scale would be one which made use of a property so selected that the scale would not depend upon the thermometric substance. Such a scale would serve throughout the entire temperature range, since no limitations due to failure or breakdown of any substance would be met. The only scales of this kind that have so far been devised will now be described.

III. Carnot's Cycle

Carnot,[1] who used a pv (pressure-volume) diagram and introduced the concept of a cycle, was interested in the problem of the efficiency of an engine. Upon what does it depend and how can it be increased? If a heat engine receives an amount of heat Q and does an amount of work W, its efficiency is defined as W/Q.

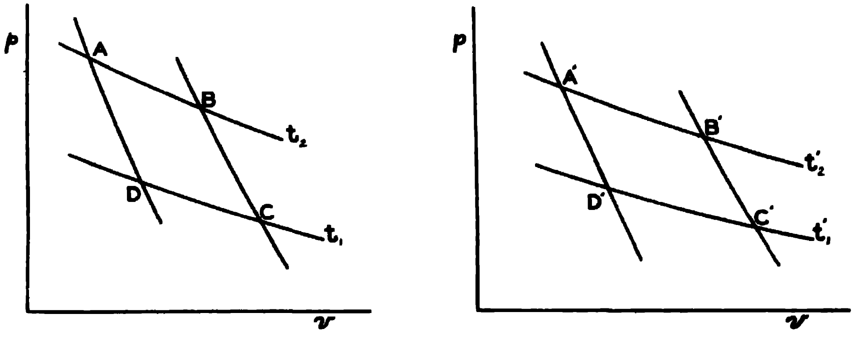

FIG. 1. Carnot's cycle.

Consider an engine as operating around a cycle consisting of two isothermals, t_1 and t_2, and two adiabatics, Fig. 1, and let there be mechanical and thermal equilibrium at each point. Let there be two large heat-reservoirs, one "hot," corresponding to t_2, and one "cold," corresponding to t_1. In passing from A to B the working substance absorbs heat Q_2 from the hot reservoir; from B to C there is no heat transfer; from C to D the substance loses heat Q_1 to the cold reservoir; from D to A there is again no passage of heat. Result: the net external work W performed by the engine, equal to the area $ABCD$, must equal $Q_2 - Q_1$ by the first law of thermodynamics.

If there is a second engine (using a different substance) working between the same two reservoirs and *any* two adiabatics we will have similarly that

$W' = Q_2' - Q_1'$. Since the processes are reversible, we may couple one working directly with the other working in reverse.

Now let us choose the strokes of the two engines so that $W = W_1'$ and let the first work directly while the second works in reverse. Net result: the hot reservoir loses $Q_2 - Q_2'$, the cold reservoir gains $Q_1 - Q_1'$ and no work is done by the combination. Since the "substance" has performed a cycle it has suffered no change, and the *only* result has been a transfer of heat $Q_2 - Q_2'$ from the hotter to the colder reservoir. Experience (second law of thermodynamics) tells us that $Q_2 - Q_2'$ cannot be less than zero.

Similarly, if the second engine works directly and the first in reverse, we have that $Q_2' - Q_2$ cannot be less than zero and therefore $Q_2 = Q_2'$; and since $W = W_1'$ the efficiencies of the two engines are the same, and independent of the working substance. Further, considering any one engine, its efficiency is independent of its stroke, for in the previous discussion the second engine may use the same working substance as the first and its stroke may be made to be simply an extension, on the diagram, of that of the first engine, etc. Therefore, the efficiency of an engine working in a reversible manner is independent of stroke, material, pressure, and volume, and is therefore a function only of the temperatures of the two reservoirs, *i.e.*, of the temperature of the working substance.

$$\frac{Q_2 - Q_1}{Q_2} \quad W = f(t_1, t_2), \tag{2}$$

where t_1 and t_2 are the temperatures on *any* scale. The type of the function will, naturally, depend upon the scale adopted.

If the cycle is infinitesimal,

$$\frac{\text{area}}{Q} = f(t, t + dt). \tag{3}$$

Since area $= 0$ when $dt = 0$ it can be shown that

$$= dt f_1(t) = F dt, \tag{4}$$

where F is "Carnot's function" and Q is the heat that must be added to keep the temperature constant as the substance expands.

Any scale which employs the efficiency of a reversible heat engine as the thermometric property is therefore independent of the working substance and is known as a "thermodynamic scale."

IV. Kelvin's Original Thermodynamic Scale

William Thomson, later Lord Kelvin,[2] seized upon Carnot's principle to define a scale of temperature. Since the efficiency of a "Carnot engine" is a function of the temperatures of the reservoirs and of nothing else, Lord Kelvin proposed to number temperature intervals proportional to increments in efficiencies. Thus

$$\frac{Q_1 - Q_0}{Q_1} = \frac{Q_2 - Q_1}{Q_2} = \frac{Q_n - Q_{n-1}}{Q_n} = \frac{q - 1}{q} \text{ (an arbitrary constant),}$$

where the subscripts are the number of degrees above some arbitrary reference temperature θ_0, Fig. 2. From the above,

$$\frac{Q_n}{Q_{n-1}} = q \quad \text{and} \quad \frac{Q_n}{Q_0} = q^n$$

or

$$n = \frac{\log Q_n - \log Q_0}{\log q},$$

and the temperature

$$\theta = \theta_0 + n = \theta_0 + \frac{\log Q_n - \log Q_0}{\log q}. \tag{5}$$

The ratio Q_n/Q_0 is the same for all substances and may be found by experiment. Since θ_0 and q may be arbitrarily selected, θ can be evaluated.

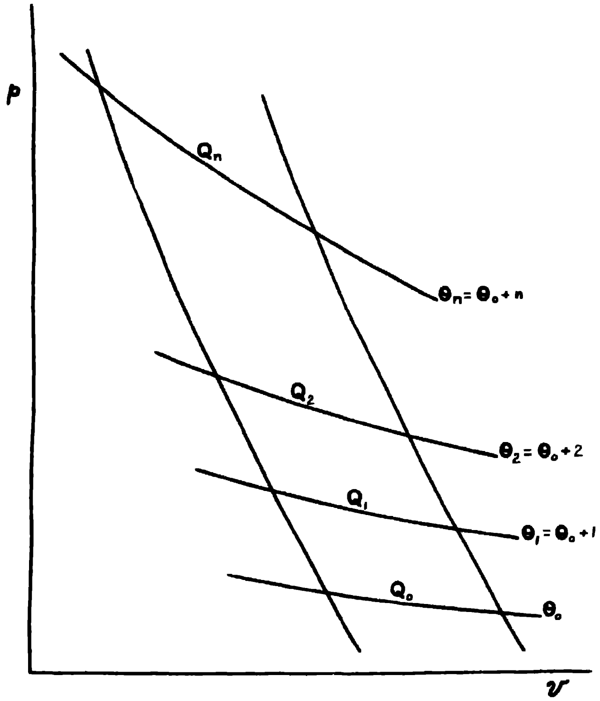
p
Q_n
$\theta_n = \theta_0 + n$
Q_2
$\theta_2 = \theta_0 + 2$
Q_1
$\theta_1 = \theta_0 + 1$
Q_0
θ_0
v

FIG. 2. Basis of Kelvin's logarithmic scale.

If the ice point be selected as the temperature to which the arbitrary value θ_0 is to be assigned, and if we wish to have a centigrade scale, *i.e.*, 100 degrees in the fundamental interval from the ice to the steam point, q must be chosen so that

$$\frac{Q_{\text{steam}}}{Q_{\text{ice}}}. \tag{6}$$

For temperatures below θ_0, $Q_n < Q_0$ and, as Q_n approaches 0, θ approaches the value $-\infty$. For temperatures above θ_0, as Q_n increases θ approaches the value $+\infty$. The efficiency for $\theta > \theta_0$ is

$$\frac{Q_n - Q_0}{Q_n} = 1 - \frac{Q_0}{Q_n} = 1 - q^{-n}.$$

Therefore $\theta = +\infty$ for an efficiency of 1. Similarly for $\theta < \theta_0$ the efficiency is $1 - q^n$. Therefore $\theta = -\infty$ for an efficiency of 1.

The above discussion holds for any finite value assigned to θ_0. The actual scale becomes definite as soon as a value is assigned to θ_0. Kelvin put $\theta_0 = 0$.

This scale did not appeal to many people because there is no similarity between the numbers assigned to temperature on this scale and on the ordinary centigrade scale. It has, however, the virtue of emphasizing the fact that when we attain a temperature of say 0.001° above absolute zero (on Kelvin's final scale), we are still far from the lowest temperature attainable.

Kelvin's first scale can be derived in another way. Let Carnot's function F be a constant, *i.e.*, this is the *definition* of this scale of temperature θ. In an infinitesimal cycle

$$\frac{\text{area}}{Q} = Fd\theta = \frac{dQ}{Q},$$

$$\log\left(\frac{Q}{Q_0}\right) = F(\theta - \theta_0)$$

or

$$\theta = \theta_0 + \frac{\log Q/Q_0}{F}, \tag{7}$$

where θ_0 is an arbitrary number assigned to some selected thermal state and Q_0 is the heat absorbed at θ_0 in the expansion between the two adiabatics. F may be given any constant value and corresponds to log q in Equation (5).

V. The Kelvin Scale

It is evident, then, that an indefinite number of temperature scales may be based on the efficiency of a reversible engine (thermodynamic scales) depending on the values arbitrarily assigned to θ_0 and F, to θ_0 and some second thermal state, or to F and the interval between two selected thermal states. Let us now consider the problem of making a good selection.

The coefficient of change with temperature of any property, a, with temperature, t, is as follows, where α is the coefficient with reference to the temperature t_0:

$$a = a_0(1 + \alpha[t - t_0]) \quad i.e., \alpha = \frac{a - a_0}{a_0(t - t_0)}. \tag{8}$$

In general, α is a function of t. Obviously α is a constant on the scale *defined by Equation (8)* since on this "a" scale equal increments in t are defined as corresponding to equal increments in the property a. The corresponding coefficient, β, of any other property, b, is then given by

$$\beta = \frac{b - b_0}{b_0(t - t_0)} = \frac{a_0(b - b_0)}{b_0(a - a_0)}\alpha$$

on the scale of "a." Only if $(b - b_0)/(a - a_0)$ is the same for all temperatures is β independent of the temperature.

The absolute zero of this scale (the number obtained by putting $a = 0$) is $t = t_0 - 1/\alpha$. This absolute zero has no relation to the number obtained for the lower limit of temperature. In general as heat is withdrawn a point is reached at which a ceases to change and the scale becomes useless.

Now it so happens that on our ordinary centigrade scale α is very nearly a constant for a large number of physical properties, such as the coefficient of linear expansion, the mean kinetic energy of the molecules of a gas, etc. It was desirable, therefore, from this standpoint, as well as to overcome psychological objections to any change, to select a thermodynamic scale which agreed approximately with the ordinary centigrade scales. Now from Equation (4)

$$\text{area} = QFdt$$

and also
$$\text{area} = \left(\frac{dp}{dt}\right)_v dt(v_2 - v_1);$$

hence
$$QF = \int\left(\frac{dp}{dt}\right)_v dv \text{ for an isothermal change.}$$

Joule applied this to the change of state, using Regnault's experiments on water and steam, and to his own experiments on the free expansion of a gas. In both cases he found that on the ordinary centigrade scale $1/F$ was very closely $t + 273$. When Joule wrote Thomson about the value he had found for the Carnot function, the latter realized that by choosing F to approximate $1/(t + 273)$ a thermodynamic scale would be obtained which approximated the ordinary centigrade scale.

Kelvin's final thermodynamic scale, known simply as the Kelvin Scale, is the only one of its kind that has ever been actually used.* It was arrived at as follows:

Kelvin defined θ_m/θ_n as equal to Q_m/Q_n because then
$$\frac{Q_n - Q_m}{Q_n} = \frac{\theta_n - \theta_m}{\theta_n}$$

and for an infinitesimal area
$$\frac{\text{area}}{Q} = \frac{d\theta}{\theta} = F dt,$$

where dt is the difference in temperature between the two reservoirs as found with an ordinary centigrade thermometer. If now $d\theta$ is chosen equal to dt, then $\theta = 1/F \doteq t + 273$.

Kelvin's final scale becomes definite as soon as a definite number is assigned to some one thermal state, or a definite number is assigned to the interval between two thermal states. For if θ_n is given, $\theta_m = (Q_m/Q_n)\theta_n$ and may be found by experiment. If $\theta_n - \theta_m$ is given
$$\theta_m = \frac{Q_m}{Q_m - Q_n}(\theta_m - \theta_n)$$

and may again be found by experiment.

The practical advantages of this scale are that (1) $\theta = t + 273$ approximately if t is the temperature on an ordinary centigrade thermometer and (2) as the efficiency
$$\frac{Q_n - Q_m}{Q_n} = \frac{\theta_n - \theta_m}{\theta_n}$$

approaches unity, θ_m approaches zero and there are no negative numbers.

A limitation of this scale is that if we make the fundamental interval from the ice point to the steam point 100 degrees, the actual temperature of the ice point is subject to experimental determination and can therefore never be *exactly* known. (The experimental value is close to 273.16 and the actual value is almost certainly between 273.1 and 273.2.)

On the other hand if we assign 273 (or even 273.16) to the ice point, as proposed by Giauque,[3] the number of degrees in the interval from the ice point to the steam point becomes subject to experimental determination and will not be exactly 100.

Kelvin wisely chose to assign 100 degrees to the fundamental interval rather than to assign a definite number to the ice point. On this scale, known simply as the Kelvin Scale, temperatures are designated as "°K" and customarily denoted by the symbol T. The ice point is denoted by T_0.

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* The Rankine Scale is essentially the same scale. Temperatures on the Rankine Scale are simply 9/5 of temperatures on the Kelvin Scale.

It may be of interest to compare the numbers, T, for a few temperatures on the Kelvin Scale with the corresponding numbers, L, for the same temperatures on Kelvin's first (logarithmic) scale. Taking the ice point as 273.16 °K,

$$L = 100\frac{\log T - \log 273.16}{\log 373.16 - \log 273.16} \quad 738 \log T - 1798.$$

A few values are given in Table 1.

Table 1. Conversion Table: Kelvin Scale to Logarithmic Scale.

		T	L
		100	-322
10^6	2630	10	-1060
10^5	1892	4.22	-1336
10^4	1154	1	-1798
3673	833	0.1	-2536
1336	509	0.01	-3274
1000	416	0.005	-3497
373.16	100	0.001	-4012
273.16	0	0	

On the logarithmic scale therefore, the progress from the attainment of 4.22 °K (the normal boiling point of helium) to the attainment of 0.005 °K (reached early in 1935) is recorded as progress from -1336 to about -3500 °L. This represents a tremendous advance, to be sure, but no more an approach to the lower end of the scale than the progress at the other end from the melting point of gold, 1336 °K, to that of tungsten, about 3700 °K, is an approach to the upper end of the scale.

If we write $t = T - T_0$, t is the temperature on a scale which is called the Thermodynamic Centigrade Scale. Any temperature *interval* has the same value when expressed on this scale as when expressed on the Kelvin Scale. When using the Thermodynamic Centigrade Scale one is simply expressing the number of Kelvin degrees that a particular thermal state is above or below the ice point. The International Temperature Scale,[4] which will be discussed later on, is a practical scale which "conforms with the Thermodynamic Centigrade Scale as closely as is possible with present knowledge."

If the only thermometer which would yield temperatures on the Kelvin Scale were a reversible heat engine, the scale would have no practical importance. However, if we had a gas which rigorously obeyed Boyle's law and which suffered no change of internal energy u during a change of volume at a constant temperature, then a given mass of this gas would obey the law $pv = kT$, where T is now the Kelvin temperature. This gas, which is called an ideal gas, when used in either a constant-pressure or constant-volume gas thermometer, would yield the Kelvin Scale directly.

The two conditions of ideality may be written

$$(pv)_t = \text{constant and } \left(\frac{du}{dv}\right)_t = \lambda = 0.$$

VI. Reduction of the Scale of a Real Gas to the Kelvin Scale

1. The Joule-Thomson Effect in Gases. Gay-Lussac and later Joule made experiments which seemed to show that if a gas expands from one vessel into another vessel previously empty, the first vessel loses just as much heat as the second one gains.

Gay-Lussac used two globes, each of about 12 liters capacity, and each containing a thermometer. One vessel was exhausted and the other contained air at atmospheric pressure. On opening a connecting stopcock, one thermometer rose 0.58° while the other fell 0.61°. Joule placed two copper vessels, connected with a pipe, in a stirred water calorimeter. One vessel was exhausted and the other filled with air at 22 atmospheres. On opening a stopcock in the connecting pipe no appreciable rise in the temperature of the calorimeter was found.

Thomson realized that it was important to repeat Joule's experiments and to measure accurately the heat required to keep the temperature of a gas constant while it was expanding. If $Q = \int p dv$ exactly there are two consequences: (1) the change $(du)_t$ in the internal energy u is zero, *i.e.*, u is a function of temperature only, and (2) $T = t + 1/\alpha$, where t is the temperature on the centigrade constant volume or constant pressure scale based on this gas and α is the coefficient of change of the pressure or volume referred to the ice point. He proposed a modification in Joule's experiment, which has come to be known as the porous plug experiment. The idea is to force a continuous stream of gas through a porous plug under conditions of no inflow or outflow of heat, the gas passing thus from a condition of high pressure to one of low pressure. If the rate of flow is kept small, the effect of the directed kinetic energy is negligible. If any change of temperature is noted, a calculation can be made as to how much heat must be added to bring the gas back to its original temperature. Thus an isothermal process may be studied.

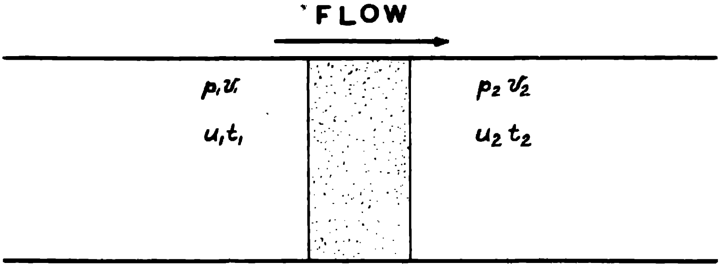

FIG. 3. Illustration of the Joule-Thomson porous plug experiment.

In Fig. 3, let $p_1 > p_2$. p = pressure; t = temperature; v = volume of unit mass; u = internal energy of unit mass.

The numerical subscripts refer to the condition of the gas, while the letter subscripts indicate that the property denoted by the subscript is held constant. Thus c_p is the specific heat at constant pressure, etc. Small letters refer to unit mass of gas. As unit mass of gas passes through the plug the net work done on the gas is equal to the increase in the internal energy, since $\Delta Q = 0$.

$$p_1v_1 - p_2v_2 = u_2 - u_1. \tag{9}$$

In order to restore the temperature to t_1, keeping the pressure p_2, the heat* to be added is

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* In another form of the experiment, heat is added during the experiment and the amount so regulated that the temperature of the gas on the two sides of the plug is the same. In this case measurement of the rate of gas flow and heat input yields the product μc_p.

$$c_p(t_1 - t_2) = u_2' - u_2 + p_2(v_2' - v_2), \tag{10}$$

where u_2' and v_2' refer to pressure p_2 and temperature t_1.

Substituting in Equation (9) the value of u_2 from Equation (10)

$$u_2' - u_1 = p_1v_1 - p_2v_2' + c_p(t_1 - t_2), \tag{11}$$

i.e.,

$$du_t = -d(pv)_t - c_p dt. \tag{12}$$

Thus, if Boyle's law holds, *i.e.*, if pv is a constant at uniform temperature, and if $t_2 = t_1$ in the porous plug experiment, $du = 0$ for an isothermal change and u is a function only of t. Otherwise du may be evaluated from the observations of Δt and $\Delta(pv)_t$.

Thomson showed how to calculate the numerical value of T for any one temperature by means of this experiment.

$$(du + pdv + vdp)_t = -c_p dt \tag{13}$$

Since increase in u = heat added (Δq) + work done on the gas $(-pdv)$

$$du = \Delta q - pdv \tag{14}$$

$$\left(\frac{\Delta q}{dp} + v\right)_t = -c_p\frac{dt}{dp} = -\mu c_p,$$

where μ is the "Joule-Thomson coefficient."

$$\frac{\text{area}}{Q} = \frac{dT}{T},$$

where Q is the heat added to keep the temperature constant as pressure is decreased from p_1 to p_2

$$Q = -\left(\frac{\Delta q}{dp}\right)_t dp,$$

$$\text{area} = \left(\frac{dv}{dT}\right)_p dTdp;$$

$$\therefore \left(\frac{\Delta q}{dp}\right)_t = -T\left(\frac{dv}{dT}\right)_p$$

Hence

$$-T\left(\frac{dv}{dT}\right)_p + v = -\mu c_p;$$

$$-\frac{1}{T}\left(\frac{dT}{dv}\right)_p + \frac{v}{T^2} = -\frac{\mu c_p}{T^2}.$$

Integrating with respect to T

$$\left[\left(\frac{v}{T}\right)_2 - \left(\frac{v}{T}\right)_1\right]_p = \int_1^2 \frac{\mu c_p}{T^2}dT. \tag{15}$$

Suppose we measure t on the scale based on the expansion at constant pressure of the same gas used in the porous plug experiment, *i.e.*, $v = v_0(1 + \alpha t)$ is the definition of this scale, where α is a constant and v_0 is the volume at the ice point, $t_0 = 0°$.

$$\frac{v}{t + 1/\alpha} = v_0\alpha = \text{a constant}$$

and

$$\left[\left(\frac{v}{t + 1/\alpha}\right)_2 - \left(\frac{v}{t + 1/\alpha}\right)_1\right]_p = 0.$$

Now, since T is known to be nearly $t + 1/\alpha$ [cf. Equation (15)], μ is a very small quantity, or conversely if it is granted that μ is a small quantity, $T = t + 1/\alpha$ approximately.

As a first approximation t may be replaced by $T - 273$ in the empirical relation expressing μ as a function of t and p found from the porous plug experiment. The integration of Equation (15) between two definite temperatures, say the ice and steam points, then yields

$$\left[\left(\frac{v}{T}\right)_2 - \left(\frac{v}{T}\right)_1\right]_p = J_2 - J_1.$$

1. Applying to the limits 0° and 100 °C and defining $T_{\text{steam}} - T_{\text{ice}} = 100$,

$$v_{100} = v_0(1 + 100\alpha) \text{ by definition.}$$

$$\frac{v_0(1 + 100\alpha)}{T_0 + 100} - \frac{v_0}{T_0} = J_{373} - J_{273}$$

$$\begin{aligned} T_0 &= \frac{1}{\alpha} + \frac{T_0(T_0 + 100)}{100 v_0 \alpha}(J_{373} - J_{273}) \\ &= \frac{1}{\alpha} + \frac{273 \times 373}{100 v_0 \alpha}(J_{373} - J_{273}) \\ &= \frac{1}{\alpha} + \epsilon_0, \end{aligned}$$

where ϵ_0 is a very small quantity found from the porous plug experiment.

2. Applying to the limits 0° and t °C

$$v = v_0(1 + \alpha t)$$

by definition of t at constant pressure. Let

$$T = T_0 + t + \delta, \tag{16}$$

$$\frac{v_0(1 + \alpha t)}{T_0 + t + \delta} - \frac{v_0}{T_0} = J_{t+273} - J_{273}.$$

Substitute

$$T_0 = \frac{1}{\alpha} + \epsilon_0,$$

$$\delta = \epsilon_0 \alpha t - \frac{273(t + 273)}{v_0}(J_{t+273} - J_{273}).$$

We may now as a second approximation use the relation found from the first calculation instead of the relation $T = t + 1/\alpha$ and repeat the calculation to secure a more exact relation etc. Actually it turns out that the first approximation is sufficient. Measurements of α and μ for a number of gases yield the result that the ice point is between 273.1 and 273.2 on the Kelvin Scale.

The calculation is valid, of course, only for values of t at which the empirical formula for μc_p holds, namely where experiments can be made, and where the approximation $t = T - 273$ is justified; namely, where the gas does not depart very far from Boyle's law.

It is to be noted that the porous plug experiment measures a single quantity which depends on the departure of the gas from both conditions of ideality. A knowledge of μ and c_p enables us to correct the results obtained with the constant pressure form of gas thermometer.

The equation, corresponding to (15), for the constant-volume thermometer is

$$\left[\left(\frac{p}{T}\right)_2 - \left(\frac{p}{T}\right)_1\right]_v = \int_1^2 \frac{\lambda}{T^2} dT.$$

Determinations of $\lambda = (du/dv)_t$ in the range of pressures of interest in gas thermometry indicate that λ is small.

2. **Berthelot's Method.** Berthelot devised a method which does not require a knowledge of μc_p or λ and is the one used in correcting practically all gas thermometer measurements.

The absolute temperature shown by a thermometer filled with any real gas defined by the relation

$$pv = \text{constant} \times \text{temperature} \tag{17}$$

may be denoted by T_v or T_p according as the volume or the pressure is kept constant. For an ideal gas we should have

$$T_v = T_p = T, \tag{18}$$

where T again denotes temperature on the Kelvin Scale, and the more closely the actual gas approaches the ideal state, or the smaller the departures from the specified properties of the nonexistent ideal gas, the more nearly will Equation (18) be true for the gas in question.

For the more permanent gases, *e.g.*, helium, neon, argon, hydrogen, and nitrogen, these departures are small and decrease as the density of the gas is diminished. Consequently a thermometer filled with one of these gases and used at either constant volume or constant pressure gives a first approximation to a realization of the Kelvin Scale, and the approximation improves as the density of the gas is lowered.

The corrections, $T - T_v$ or $T - T_p$, may be found from the results of auxiliary experiments on the properties of the gases which determine how far these properties depart from those assigned, by definition, to the ideal gas. Over the temperature ranges in which they have been investigated, these corrections are small (usually negligible in comparison with the precision attainable in gas thermometry).

Berthelot's method relies on measurements of compressibility at constant temperatures. It is based upon two postulates: (1) that the gas approaches the ideal state as its density approaches 0, so that $T_v \doteq T_p \doteq T$, and (2) that the extrapolation—whether graphical or analytical—from the lowest measured values of p to $p = 0$ is permissible.

The method amounts, in principle, to drawing the isothermals $pv = f(p)$ from observations at known and reproducible temperatures, and extrapolating them to $p = 0$, so as to find their intercepts on the pv axis.

From Fig. 4, $T_p \doteq T_v$ when $p =$ Let AA' and BB' be the isothermals determined by experiment at the temperatures t_1 and t_2. Then if the constant-pressure thermometer is used at the pressure p_0,

$$\frac{(T_p)_2}{(T_p)_1} \quad \frac{FE}{FC}.$$

whereas if the constant-volume thermometer is used with the pressure p_0 at the lower temperature,

$$\frac{(T_v)_2}{(T_v)_1} = \frac{OD}{OC}.$$

These ratios, obviously, approach each other as p_0 approaches 0.

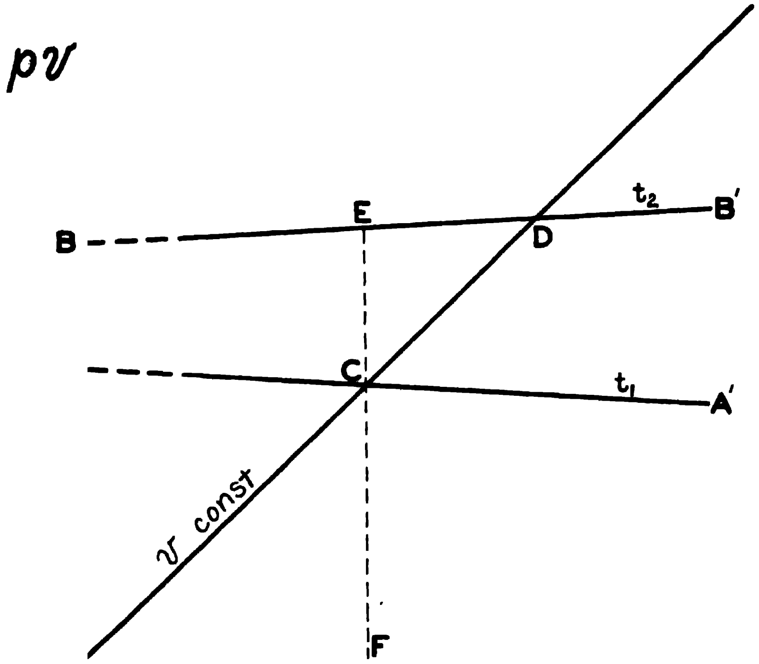

FIG. 4. Berthelot's method.

If the two postulates stated above hold for the gas used, the ratio T_2/T_1 is therefore given by OB/OA and can be found for any two temperatures.

The first postulate will hardly be questioned by anyone. The second amounts to assuming that the isothermals do not suffer any sudden changes of direction at pressures below those at which accurate measurements of $pv = f(p)$ can be made. This seems also to be subject to very little doubt. If t_1 and t_2 are any two reproducible temperatures, compressibility experiments carried out at these temperatures on the same mass of gas yield the ratio T_2/T_1 directly, without any reference to T_v or T_p.

In his paper Berthelot did the work algebraically instead of graphically. By setting up a general reduced equation, he coördinated the available experimental data on various gases, the only requirement being that the equation should hold for the low pressures used in gas thermometry.

If the compressibility data on any one gas are accurate enough and cover the desired range of temperature, the use of a general reduced equation of state is unnecessary, and the objectionable assumption of a law of corresponding states * is avoided. The two original postulates remain, and their existence should not be ignored. Nevertheless, this method is probably the most accurate available for determining the ratios of any two values of T. The constant-pressure method of

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* In the more special form announced by van der Waals it says that if the pressures, volumes, and absolute temperatures be expressed as ratios of their values at the critical point, the equation of state is the same for all substances and contains no quantities dependent on the special properties of particular substances.

gas thermometry has not been used much in recent years. The constant-volume hydrogen and helium thermometers have been used successfully below 0 °C. At moderately high temperatures, the materials used for the bulbs appear to become permeable to hydrogen and helium and to react with hydrogen, so that exact work with them has not been done above about 100 °C. For higher temperatures nitrogen is found satisfactory.

The corrections to the constant volume nitrogen scale for an initial (ice point) pressure of 1000 mm of mercury are about 0.2 °K at 700 °K and about 1 °K at 1500 °K. These corrections, being proportional to the initial pressure, are smaller for the pressures used in high-temperature gas thermometry. Thus in their work on the gold point, 1336 °K, Day and Sosman used initial pressures of 217 and 345 mm of mercury.

While a high degree of accuracy cannot be claimed for the corrections, it is to be emphasized that they are small. The corrections to the experimentally determined values of T for the melting point of gold are only about 0.2 or 0.3 °K, so that an error of even 50 per cent in these corrections is not a serious matter.

VII. High-temperature Gas Thermometry

The nitrogen constant-volume scale has been extended up to 1550 °C by Day and Sosman[5] by a monumental work during which they determined the melting point of palladium as 1549.2 °C on this scale. It is very improbable that their work will be repeated for a long time to come. The difficulties are too great. They estimate ±2° as the accuracy of this determination. The importance of their classic work can scarcely be overestimated. Their value for the palladium point yields an important check on the laws of radiation, and their determination of T for the melting point of gold, or "gold point," is largely the basis for our present high-temperature scale.

There have been a number of determinations of the gold point on various gas thermometer scales. The results of some are listed in Table 2.

Table 2.

Experimenters	Year	Value Obtained (°C)
Barus	1892	1093
Holborn and Wien	1895	1072
Holborn and Day	1901	1063.5
Jaquerod and Perrot	1905	1067.2
Day and Clement	1907	1059.3
Day and Sosman	1912	1062.4

The values obtained before the beginning of the present century are now of only historical interest. In fact only those of Holborn and Day, obtained at the Reichsanstalt in Berlin, and of Day and Sosman, obtained at the Geophysical Laboratory in Washington, should be considered. On this basis we know that the gold point is within 1°, probably within 0.5°, of 1336 °K.

The next step is to extend this scale, with the gold point = 1336 °K as a basis, to higher temperatures.

VIII. Optical Methods of Temperature Measurement

1. **The Blackbody.** Imagine a hollow enclosure impervious to heat from without. If left to itself it will come to a uniform temperature, in accordance with the second law of thermodynamics, provided there is a possibility of interchange

of heat between all parts of its inner wall. This presupposes that a portion at least of the interior surface emits and absorbs, to some extent, all *wave-lengths,* and that no portion is a perfect reflector.*

When a state of constant and uniform temperature is reached, *the radiant energy at any point inside such an enclosure is independent of the nature of the walls.* To prove this, consider the following processes:

a. Place inside the enclosure a spherical body whose surface is totally reflecting with the exception of a minute element which is totally absorbing, *i.e.,* "black." After a time there is temperature equilibrium throughout both enclosure and spherical body. In this state, the energy E_s emitted by the spherical body per unit time must equal that which it absorbs E, the latter quantity being the energy falling upon the "black" element of the spherical body and coming from the walls of the enclosure. E_s must be a property of the spherical body and must therefore remain unchanged if its temperature is not changed.

b. Now alter the character of a portion of the wall of the enclosure, keeping its temperature unchanged, *e.g.,* make it "black." The existing temperature is unaffected and therefore E_s is unchanged since the spherical body is unaffected; hence E is unchanged.

c. If the sphere is now rotated so that the black element is brought into a new position and is facing in a new direction, the temperature equilibrium is again unaffected and E_s is unchanged. That is, *the flux of radiant energy at all points and in all directions inside the enclosure is identically the same.*

It may be similarly demonstrated that the quality (as regards "polarization") and distribution of radiant energy among the various wave-lengths is likewise independent of everything except temperature. We can, in such cases, speak of the *temperature of the radiant energy.*

The radiant energy inside an enclosure at constant and uniform temperature is called "blackbody radiation." Any body which emits blackbody radiation is called a "blackbody." The energy emerging from an opening in the walls of an enclosure such as described above approaches blackbody radiation as the opening is made smaller and smaller. Such a small opening is, for all practical purposes, a blackbody.

2. Kirchhoff's Law. Consider the radiant energy E_λ of any definite wave-length λ along a line joining any element of the wall with any element of the enclosed body. In either direction it is the same and is that characteristic of a blackbody. Of the energy E_λ falling on it, the element of the enclosed body will absorb an amount $A_\lambda E_\lambda$, reflect an amount $r_\lambda E_\lambda$, and transmit an amount $t_\lambda E_\lambda$. Let

$$G_\lambda = r_\lambda E_\lambda + t_\lambda E_\lambda = (1 - A_\lambda)E_\lambda. \tag{19}$$

In the other direction the radiant energy coming from the element of the enclosed body is made up of the part emitted $(E_s)_\lambda$ and the part reflected or transmitted,

$$G_\lambda' = r_\lambda E_\lambda + t_\lambda' E_\lambda = E_\lambda - (E_s)_\lambda. \tag{20}$$

The reflected part is obviously the same in the two cases, but the transmitted parts $t_\lambda E_\lambda$ and $t_\lambda' E_\lambda$ are traveling in opposite directions. From the laws of optics, however, $t_\lambda = t_\lambda'$.

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* The existence of a perfectly reflecting portion does not affect the character of the radiant energy inside the space and therefore such a portion, if present, may be disregarded. The second of the above conditions is essential only to the process of attaining a uniform temperature.

If we define the spectral emissivity, e_λ, of a body as the ratio of the energy of wave-length λ radiated by the body to that radiated by a blackbody at the same temperature $(E_s)_\lambda = e_\lambda E_\lambda$. ($e_\lambda$ for any body is a function of both λ and temperature.)

Then $G_\lambda' = G_\lambda$ and

$$E_\lambda - (E_s)_\lambda = (1 - e_\lambda)E_\lambda = (1 - A_\lambda)E_\lambda. \tag{21}$$

Hence $e_\lambda = A_\lambda$. This is Kirchhoff's law.* Therefore a body at a given temperature emits an amount of radiant energy $(E_s)_\lambda = e_\lambda E_\lambda$, which is equal to blackbody radiation of this temperature which it will absorb, $A_\lambda E_\lambda$. This law is used in the measurement of flame temperature by the line reversal method.

3. The Laws of Radiation. There have been many investigations, both experimental and theoretical, to determine how the distribution of energy in the spectrum of a blackbody depends on wave-length and temperature. On the basis of "classical mechanics" and certain postulates regarding the mechanism of radiation Wien deduced the formula

$$J_{\lambda T} = \frac{c_1}{\lambda^5 e^{c_2/\lambda T}} \text{ Wien's Formula}$$

in which λ is the wave-length, T is the temperature in degrees K, e is the Naperian base 2.71828 ··· and $J_{\lambda T}$ is the radiant energy (of wave-length λ) per unit wave-length interval emitted per unit time by unit area of a blackbody at temperature T throughout the solid angle 2π, *i.e.*, "hemispherical radiation."

According to this formula, $J_{\lambda T}$ does not increase without limit as T increases for finite values of λ, because when $T = \infty$, $J_{\lambda T} = c_1\lambda^{-5}$. In 1900 Rubens and Kurlbaum made measurements at very long wave-lengths and found that at $\lambda = 0.005$ cm their results deviated from Wien's formula by 40 per cent at $T = 1773$ and by several hundred per cent at low temperatures. It is reported that when they wrote to Planck, who was on vacation, the latter replied on a postcard: "Try adding minus one to the denominator." This was the conception of the quantum theory.

Planck's formula,

$$J_{\lambda T} = \frac{c_1}{\lambda^5(e^{c_2/\lambda T} - 1)}, \tag{22}$$

fitted the observations of Rubens and Kurlbaum at $\lambda = 0.005$ cm within 4 per cent from $T = 85$ °K to $T = 1773$ °K.

The birth of the quantum theory occurred when Planck attempted to derive his formula theoretically and found that it could not be done without postulating that energy is radiated only in multiples of a finite quantity $\epsilon = h\nu$, h being a constant and ν the frequency.

Planck's derivation[6] is not considered valid today. However, a rigorous derivation results from the application of modern quantum statistics and our main interest is in the fact that, today, the validity of Planck's formula is not questioned. We therefore have a means of extending the Kelvin Scale upward without limit.

The maximum value of $J_{\lambda T}$ is easily found to be at

$$\lambda_{\max} = \frac{c_2}{4.9651\,T}. \tag{23}$$

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* It must be noted that Kirchhoff's law is based upon the postulate that (E_s) is a property of the body and does not depend upon the radiant energy falling upon it. Kirchhoff's law, therefore is not true for fluorescent bodies for which this postulate is not fulfilled.

Furthermore

$$\int_0^\infty J_{\lambda T} d\lambda = \sigma T^4, \tag{24}$$

which is the Stefan-Boltzmann law. Any one of the three formulas (22), (23), or (24) will yield the Kelvin scale.

The various constants involved are related as follows:

$$c_1 = 2\pi c^2 h = \frac{15}{\pi^4} \sigma c_2^4, \tag{25}$$

$$c_2 = \frac{ch}{k} = \left(\frac{h}{e}\right)\frac{cF}{R}, \tag{26}$$

and

$$\sigma = \frac{2\pi^5 c^2 h}{15 c_2^4} = 40.8026 \frac{c^2 h}{c_2^4}, \tag{27}$$

where c = the velocity of light in cm sec.$^{-1}$;
h = Planck's constant of action in erg sec.;
k = the Boltzmann constant in erg deg.$^{-1}$;
e = electronic charge in electrostatic units (e.s.u.);
F = the Faraday constant in (e.s.u.) mole^{-1};
R = the gas constant in erg deg.$^{-1}$ mole^{-1}.

4. **Optical Pyrometry.** Inasmuch as absolute measurements of radiant energy are difficult and inaccurate, whereas relative values can easily be measured with considerable accuracy, the following equation, which follows directly from Equation (22), is in the form useful for optical pyrometry.

$$R_\lambda = \frac{J_{\lambda T_1}}{J_{\lambda T_2}} = \frac{e^{c_2/\lambda T_2} - 1}{e^{c_2/\lambda T_1} - 1}. \tag{28}$$

It is evident that if we know c_2 and the value of T for some fixed point at which a blackbody emits sufficient light for the purposes of optical pyrometry, the problem of extending the Kelvin Scale upward in practice is solved. It is also evident that if we know the values of T for two suitable fixed points, a measurement of R_λ for any value of λ with an optical pyrometer will serve to determine c_2. Six such suitable fixed points have been determined by gas thermometry.[7]

The value of c_2 may also be found, using Equation (23), from a knowledge of T and λ_{max} for one fixed point. Similarly c_2 may be found from Equation (27) from measurements of σ as defined in Equation (24). Finally, c_2 may be calculated from the various atomic constants in Equation (26). The values obtained are given in Table 3 which is taken from a review [7] of the experimental data.

Table 3. Summary of Values of c_2 from all Sources.

Source	c_2 in cm deg.	Weight
$\lambda_m T$	1.4361 ± 0.0050	1
σ	1.4368 ± .0040	1
Optical Pyrometry	1.4364 ± .0020	2
Atomic constants	1.4358 ± .0015	3
Weighted mean	1.4362 ± 0.001	
Mean deviation	0.0003	

IX. The International Temperature Scale

The International Temperature Scale, unanimously adopted in 1927 by the Seventh General Conference of Weights and Measures (representing 31 nations), is based on a number of fixed points whose location on the Kelvin Scale relative to the ice point has been determined by gas thermometers. Part I of the text of the scale, given below, is self-explanatory. A few editorial corrections, not affecting the scale itself, were made in 1933.

Definition of the International Temperature Scale

1. The Thermodynamic Centigrade Scale, on which the temperature of melting ice, and the temperature of condensing water vapor, both under the pressure of one standard atmosphere, are numbered 0° and 100°, respectively, is recognized as the fundamental scale to which all temperature measurements should ultimately be referable.

2. The experimental difficulties incident to the practical realization of the thermodynamic scale have made it expedient to adopt for international use a practical scale designated as the International Temperature Scale. This scale conforms with the thermodynamic scale as closely as is possible with present knowledge, and is designed to be definite, conveniently and accurately reproducible, and to provide means for uniquely determining any temperature within the range of the scale, thus promoting uniformity in numerical statements of temperature.

3. Temperatures on the international scale will ordinarily be designated as "°C," but may be designated as "°C(Int.)" if it is desired to emphasize the fact that this scale is being used.

4. The International Temperature Scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated according to a specified procedure at the fixed temperatures.

5. The basic fixed points and the numerical values assigned to them for the pressure of one standard atmosphere are given in the following table, together with formulas which represent the temperature (t_p) as a function of vapor pressure (p) over the range 680 to 780 mm of mercury.

6. Basic fixed points of the International Temperature Scale—

	°C
(*a*) Temperature of equilibrium between liquid and gaseous oxygen at the pressure of one standard atmosphere (oxygen point) $t_p = t_{760} + 0.0126(p-760) - 0.0000065(p-760)^2$.	−182.97
(*b*) Temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure (ice point)	0.000
(*c*) Temperature of equilibrium between liquid water and its vapor at the pressure of one standard atmosphere (steam point) $t_p = t_{760} + 0.0367(p-760) - 0.000023(p-760)^2$.	100.000
(*d*) Temperature of equilibrium between liquid sulfur and its vapor at the pressure of one standard atmosphere (sulfur point) $t_p = t_{760} + 0.0909(p-760) - 0.000048(p-760)^2$.	444.60
(*e*) Temperature of equilibrium between solid silver and liquid silver at normal atmospheric pressure (silver point)	960.5
(*f*) Temperature of equilibrium between solid gold and liquid gold at normal atmospheric pressure (gold point)	1063

Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm high, having a density of 13.5951 g/cm^3, subject to a gravitational acceleration of 980.665 cm/sec.^{2} and is equal to 1,013,250 dynes/cm^2.

It is an essential feature of a practical scale of temperature that definite numerical values shall be assigned to such fixed points as are chosen. It should be noted, however, that the last decimal place given for each of the values in the table is significant only as regards the degree of reproducibility of that fixed point on the International Temperature Scale. It is not to be understood that the values are necessarily known on the Thermodynamic Centigrade Scale to the corresponding degree of accuracy.

7. The means available for interpolation lead to a division of the scale into four parts.

(*a*) From the ice point to 660 °C the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0(1 + At + Bt^2).$$

The constants R_0, A, and B of this formula are to be determined by calibration at the ice, steam, and sulfur points, respectively.

The purity and physical condition of the platinum of which the thermometer is made should be such that the ratio R_t/R_0 shall not be less than 1.390 for $t=100°$ and 2.645 for $t=444.6°$.

(*b*) From $-190°$ to the ice point, the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3].$$

The constants R_0, A, and B are to be determined as specified above, and the additional constant C is determined by calibration at the oxygen point.

The standard thermometer for use below 0 °C must, in addition, have a ratio R_t/R_0 less than 0.250 for $t=-183°$.

(*c*) From 660 °C to the gold point, the temperature t is deduced from the electromotive force e of a standard platinum *vs.* platinum-rhodium thermocouple, one junction of which is kept at a constant temperature of 0 °C while the other is at the temperature t defined by the formula

$$e = a + bt + ct^2.$$

The constants a, b, and c are to be determined by calibration at the freezing point of antimony, and at the silver and gold points.

(*d*) Above the gold point the temperature t is determined by means of the ratio of the intensity J_2 of monochromatic visible radiation of wave-length λ cm, emitted by a blackbody at the temperature t_2, to the intensity J_1 of radiation of the same wave-length emitted by a blackbody at the gold point, by means of the formula

$$\log_e \frac{J_2}{J_1} = \frac{c_2}{\lambda}\left[\frac{1}{1336} - \frac{1}{(t + 273)}\right].$$

The constant c_2 is taken as 1.432 cm degrees. The equation is valid if $\lambda(t+273)$ is less than 0.3 cm degrees.

The statement that the International scale "conforms with the thermodynamic (centigrade) scale as closely as is possible with present knowledge" is not entirely true today. The introduction to the scale stated that the scale "is to be regarded as susceptible of revision and amendment as improved and more accurate methods of measurement are evolved."

The International Conference, meeting every six years, was scheduled to consider revision of the temperature scale in October 1939, but failed to meet in 1939 on account of the unsettled political conditions. Among the revisions by which the conformity with the thermodynamic scale might be improved are (1) the substitution of Planck's formula (28) for the form of Wien's formula given in the scale, (2) the use of a slightly higher value for c_2, (3) some modification in values assigned to some of the fixed points to make departures from the thermodynamic scale smaller and more regular, (4) making the junction between the thermocouple and the resistance thermometer ranges at the freezing point of antimony instead of at 660 °C, (5) extension of the scale below −190 °C, and (6) better specifications for the standard resistance thermometer.

None of these revisions, with the exception of (4) and (5), would make the scale more useful. Its greatest usefulness lies in the fact that its universal use has practically eliminated ambiguities in the specification of temperatures. If and when the scale is modified, the resulting differences will be known and conversion from the 1927 scale to the modified scale can be easily made. If for some time during and after such a modification, people are careful to state on which scale temperatures are being specified, no confusion should occur. The first requirement of any scale is that it provide means by which any thermal state may be unambiguously specified.

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The Temperature of the Human Body in Health and Disease*

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As far as I know, this is the first occasion on which the biologists, physiologists and clinicians have been asked to take part in a Symposium sponsored chiefly by physicists and engineers. We believe that we have something to contribute to the subject of temperature and are much flattered that our contributions are considered of sufficient importance to be included in this program. My own task this afternoon is to show that many of the laws of physics are well illustrated in our own bodies. As a matter of fact, there are on the program 22 papers that deal more or less directly with the question of body temperature and its control. It is safe to say that the advances in knowledge have been due chiefly to the work of the men who are presenting papers in subsequent sessions. There have, of course, been important contributions in Europe, but I believe that most of the best work is now being done in this country. There has been during the last few years a great revival of interest in this subject, largely on account of the introduction of more exact physical methods. In this connection I would like to quote the stirring words of Magendie, written in Paris as long ago as 1836 as an introduction to his "Elements of Physiology": "In a few years physiology, which is already allied with the physical sciences, will not be able to advance one particle without their aid. Physiology will acquire the same rigor of method, the same precision of language and the same exactitude of result as characterize the physical sciences. Medicine, which is nothing more than the physiology of the sick man, will not delay to follow in the same direction and to reach the same dignity. Then all those false impressions which, as food for weakest minds, have so long disfigured medicine, will disappear."

The range of temperatures discussed in this Symposium is vast. Man occupies a relatively narrow zone. True, he is exposed to weather that is extremely hot in the tropics or in industry, and extremely cold in the Arctic regions; but man really lives, not in the air, but inside his own skin. The active cells of the body are all beneath the surface, the most important of them a long way below the surface. In the process of evolution, man and the other mammals have arrived at a certain optimal temperature for the body cells, and the organism strives to preserve this temperature as closely as possible. Our problem is to define the limits of this zone, to describe the mechanism by which the optimal temperature is maintained, and to give an idea of the disastrous effects when the temperature control fails.

It seems like a waste of time to talk about the normal body temperature when everyone owns a clinical thermometer with a nice little arrow showing the exact level of the normal. Many people do not merely own clinical thermometers, but worship them, and particularly do they worship the little arrow, guiding the activities of the family by this fetish. In their minds anything above the little arrow means fever. Doctors realize that the temperature may be half a degree or more above the arrow without its being of significance; and the clinical thermometer proves indispensable in the practice of medicine since, with all its limitations, it is accurate enough for ordinary purposes.

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When, however, we come to a finer study of the body temperature and try to use its changes quantitatively for scientific purposes, we encounter great difficulties. The literature is full of confusion. My hardest task during these last six months has been to find the average normal body temperature and the average diurnal range. All the best workers who have written on this subject have carefully avoided giving these figures and I sympathize with them. The best that we can do is an approximation, with a recognition of the fact that there are many individual variations. In viewing the whole subject of body temperature, I am not certain as to which is the more striking—the narrowness of the zone of normal temperature, or the breadth of the zone in which life is possible. In Fig. 1 I have tried to show a scale of body temperatures; the normal zone for the internal or rectal body temperature centers at about 37 °C (98.6 °F) with a spread of about 0.6 °C, or 1.0 °F, above and below this central point. The febrile diseases give temperatures up to 40 or 41 °C, seldom above 41 (106 °F). There seems to be a level of secondary regulation at about 40.5 °C which prevents the body, even in serious infectious diseases, from rising into the danger zone. In artificial fevers produced for therapeutic purposes, temperatures of 41.5 °C (106.8 °F) are sometimes maintained for five or even ten hours. Higher temperatures are found in heat-stroke, in certain diseases of the central nervous system, and occasionally in infectious diseases or after drugs. The upper limit of survival is said to be about 45 °C, and if this level is maintained for only a short time recovery is possible, though not probable. The lower cold zones have only recently been explored therapeutically and they will be discussed in one of the papers in this Symposium. Survival is possible after a body temperature as low as 24 °C (75 °F). Here, then, is a wide range, and man may be considered poikilothermic at times but usually he is strictly homeothermic as far as the interior of his body is concerned.

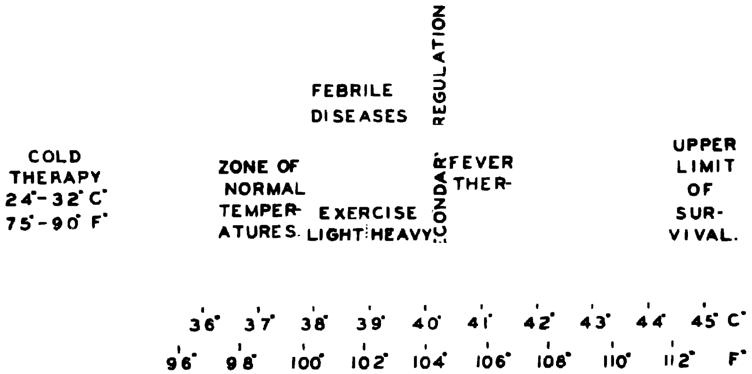

FIG. 1. The range of internal temperatures in man.

It is hardly fair to speak of *the* temperature of the body. There is no one temperature of the body. Mouth temperature ranges about 0.6 °C lower than the rectal temperature. The average temperature of the surface is much lower than the internal. In warm environments the naked skin averages 2 °C lower than the rectal reading. In cold environments, not quite cold enough to produce chills, it averages 6.5° lower. Some parts of the surface, particularly the toes, are often as cold as, or even colder than, the air. Inasmuch as about 17 kg of body tissue lie within a centimeter of the surface, it is obvious that this large mass may be much colder than the interior. Since the interior is warm and the surface cold, there is a temperature gradient which may extend four to seven, or even ten, centimeters deep. There are some organs in the interior of the body such as the liver, which are one or more degrees warmer than the rectal temperature. Heat is produced in the muscles and large organs of the body; it is lost only at the surface.

One may list the factors affecting body temperature, roughly in their order of importance, as follows:

(1) Febrile diseases
(2) Severe muscular exercise
(3) Moderate muscular activity
(4) Time of day
(5) Age
(6) Environmental temperature
(7) Individual variation, especially in children
(8) Sleep
(9) Menstruation
(10) Emotion

There is an enormous literature on the average body temperature, but very few measurements which do not involve many of these factors. Only a few of the studies are suitable for the determination of the average normal. Some of the investigators have used rectal temperatures; others oral temperatures, which average about 1 °F (0.6 °C) lower than the rectal, and are fairly reliable if taken with great care. Most authors give the average rectal temperature as 37.0 °C (98.6 °F), and the range of variation from 0.4 to 1.4 °C. Reimann,[1] in a review of this subject, says, "It appears that the oral temperature of about 60 per cent of normal adult persons rests between 36.8 °C (98.2 °F) and 37.2 °C (98.9 °F)." The spread beyond these levels is considerable in both directions with the incidence of probability diminishing toward the extreme of 36.1 °C (97 °F) on one hand, and 37.9 °C (100.2 °F) on the other. Benedict and Carpenter,[2] in careful studies made in their calorimeter and published in 1910, found in one group an average of 36.67 °C (98 °F) of oral temperatures during the day, with an average range of 0.82 °C; and in another group studied only in the daytime, an average of 36.82 °C in those who received food, and 36.67 °C in those without food. In the first group the average range was 0.96 °C, with a minimum in the early morning and a maximum in the late afternoon or early evening. Those without food had an average range of 0.77 °C, and the maximum temperature was frequently observed in the forenoon. Some of the individuals showed ranges of 1.3 or even 1.6 °C. Benedict and Carpenter conclude that the point 37.0 °C (98.6 °F), in common usage, is too high, and that fluctuations of as much as 1.1 °C (2 °F) above and below 37.0 °C (98.6 °F) may well be within the range of physiological limits.

Benedict and Talbot[3] have published a table showing the average rectal temperature of boys and girls from the age of three-quarters of an hour to 12½ years. These temperatures have been charted in Fig. 2. The number of individuals in each group ranged from 2 to 44, but most of the averages are based on more than

15 observations on more than 5 individuals. Unfortunately there are only two boys 5 years old, and the authors do not believe that the low value for these two boys is characteristic of that age. It is interesting to note that there is very little difference between the boys and the girls. Benedict and Talbot have called attention to the peak at the age of ten months to two years when metabolism is at its highest. The fall in metabolism after this peak is partially confirmed by the temperature measurements of Lewis, Kinsman and Iliff[4] made on normal children taking basal metabolism tests in Denver. In Fig. 2 I have charted the averages in all tests where rectal temperatures are recorded. A few of the groups consist of only four or five individuals.

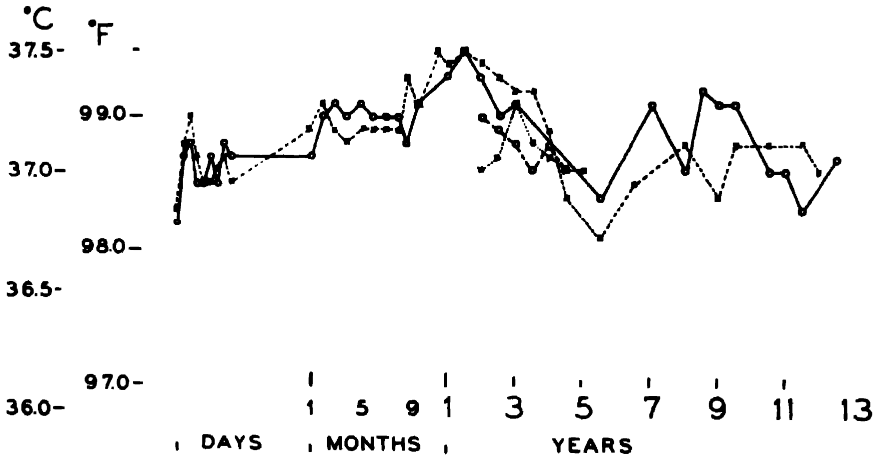

FIG. 2. Average temperatures of boys (continued line) and girls (dashed line) taken from the monographs of Benedict and Talbot. These were rectal temperatures in children having basal metabolism tests. Similar temperature readings made by Lewis, Kinsman and Iliff, in Denver, have been made. They record rectal temperatures only for boys (heavy dashed line) and girls (dotted line) between the ages of 2 and 5. The very low dot at the age of 5 is the average for the only two boys at this age in the series of Benedict and Talbot.

We ourselves have had the opportunity of studying the normal rectal temperature under almost ideal conditions during our experiments in the respiration calorimeter of the Russell Sage Institute of Pathology.[5] We have, during the last twenty-five years, made observations on a large number of men and a fairly large number of women under basal conditions, that is, between the hours of 11 A.M. and about 2 P.M., the last food having been taken at 7 o'clock the previous evening. The subjects were all lying practically motionless in a comfortable environment, awake, though perhaps a little drowsy. We used an electrical resistance thermometer, accurate within one hundredth of a degree, inserted 12 cms into the rectum at least three-quarters of an hour before the first reading was made. The readings are charted in the histogram in Fig. 3. It will be observed that the peak of the curve comes at 36.90, with a spread between 36.2 and 37.6. Most of the subjects were young men, but there are included in this group a number of boys twelve to sixteen years of age, and six old men 77 to 83 years of age. The women were all young. Their average body temperature was the same as that of the men. This is contrary to the opinion usually expressed that women have a slightly higher temperature. If the observations had been made with the ordinary rectal clinical thermometer inserted about 4 cms for two to four minutes, the readings would probably have been about 0.2 °C lower. If these people had not gone without breakfast and had not remained motionless, their readings would probably have been 0.2 °C or more higher.

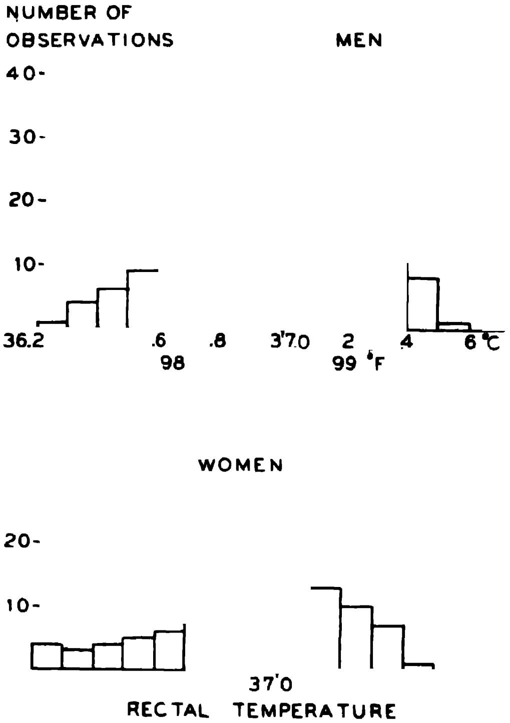

FIG. 3. Distribution of rectal temperature readings made on normal men and women in the respiration calorimeter of the Russell Sage Institute of Pathology in the years between 1913 and 1939.

Under ordinary conditions there is a diurnal variation of the temperature with a difference of about 1 °C between the lowest point obtained between 2 and 6 A.M. and the highest point around 4 to 6 P.M. In Fig. 4 we have drawn a heavy line showing part of this diurnal curve and have sketched in the readings taken on the men under basal conditions without food. It will be observed that in the first hour there is a drop of 0.1 or 0.2 °C, and that in the second hour the temperatures are almost level or else falling slightly. Thus it would seem that the diurnal variation tends to disappear when people are kept very quiet without food.

In some experiments we gave a large amount of meat, about 660 grams of chopped beef containing twice as much protein as the average man eats in a day. After this meal there was a marked rise in metabolism, the so-called specific dynamic action of food, and in most cases a slight rise in rectal temperature, followed by a fall. A relatively small meal, consisting of 100 to 200 grams of glucose, caused no rise in body temperature, but checked the tendency toward fall.

Our figures merely confirm the careful studies published by Burton and Murlin in 1935.[6] Their calorimeter was similar to ours, but they followed the surface temperatures by means of jackets and bands of cloth containing resistance wires. Their protein meals were smaller, some of the carbohydrate meals larger. They found in the basal experiments, before food, a slight drop of rectal temperatures in the first hour, a levelling in the second hour. The average surface temperature fell 0.08 °C in the first hour, 0.25 °C in the second. After the meals in the middle of the day, the rectal temperature rose on an average 0.26 °C in the first hour and levelled off in the second. The surface temperature, however, rose on an average 0.79 °C in the first hour, 0.18 in the second, and fell a little in the third. They believe that the ingestion of food causes an increase in blood circulation throughout the body, not merely in the digestive organs.

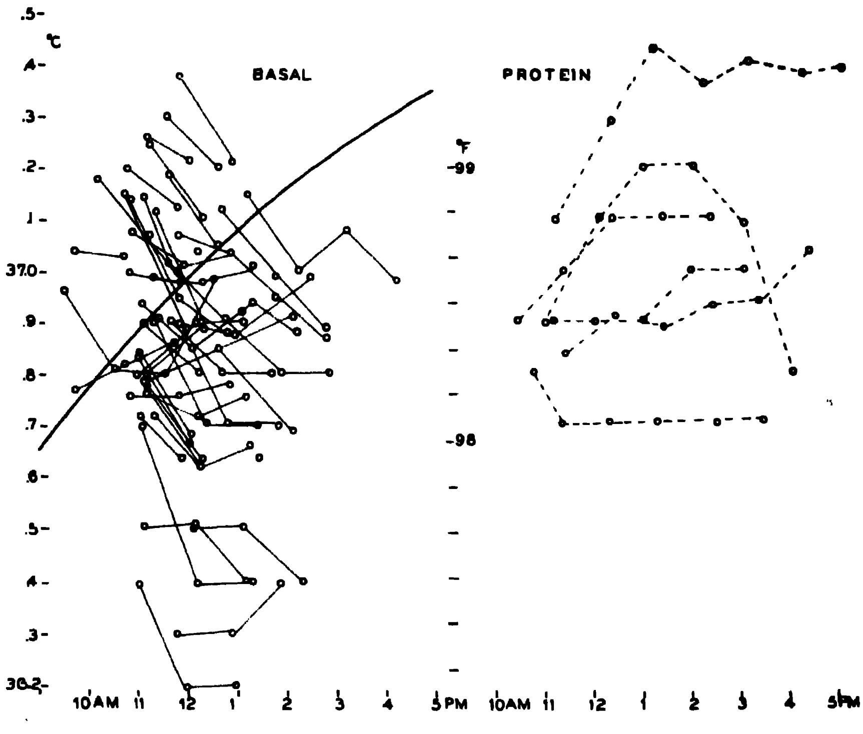

FIG. 4. Lines showing the changes in rectal temperature during the hours when normal controls were in the calorimeter. In the left-hand figure, which shows the results on subjects without food since 7 o'clock the previous evening, a heavy curve has been drawn representing the usual diurnal change in temperature. In the right-hand figure is shown the transient rise in rectal temperature which occurs after a large meal consisting of about 660 grams of chopped beef.

Mild exercise causes a slight rise in body temperature, but the effects of severe exercise are striking. This is illustrated in Fig. 5, which shows what happened when two of the doctors on our staff played a violent game of squash-rackets for three periods of 12 minutes each, with short pauses between each period, during which measurements were made.[7] The results were almost exactly the same on the two men; the figure charted for one of them shows that the rectal temperature rose from about 37.5 to 39 °C in 36 minutes. It is obvious that heat production, which increased about tenfold during the game, exceeded the heat loss even though there was an enormous vaporization of sweat. When the men rested, heat loss, chiefly through vaporization, exceeded production and rectal temperature fell to its normal level in 35 minutes. Incidentally, I would like to point out that the

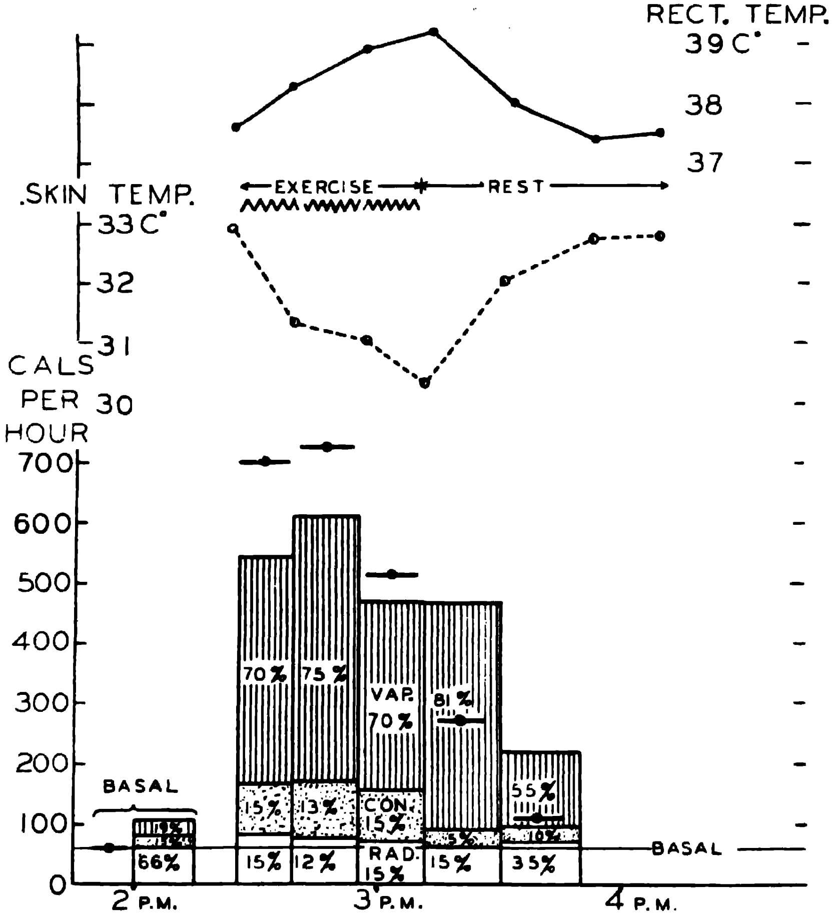

FIG. 5. Diagram showing the effect of violent exercise. Normal control played three games of squash-racquets. The rectal temperature rose sharply to fever levels; the skin temperature fell. The round dots with horizontal lines through them show the estimated heat production, and the columns the estimated heat loss.

average skin temperature, which was 33 °C before the game started, fell to 31.5 °C in 36 minutes. This follows the general rule that skin temperature drops when the body gives off more heat.

Cold environmental temperatures have a profound effect on surface temperatures when the subjects are quiet; and if the cold is extreme very low body temperatures may be attained, as in the recent dramatic studies on cold therapy.

Under ordinary conditions, however, the effect of moderate cold on rectal temperature is relatively slight. Using the Sage calorimeter,[8] we made a series of observations on two normal men studied naked and motionless in the calorimeter with environmental temperatures ranging from 22 °C (73 °F) to 35 °C (95 °F). At 23 °C the men were on the verge of shivering. At temperatures above 31 °C they were sweating. These men were studied naked. Had they been clothed there would have been less change in the rectal temperature and much less change in the surface temperature. Clothing tends to keep the surface warmer in cold environments, and light clothing keeps the surface cooler in warm environments.

During the menstrual cycle there is a slight but fairly constant change in body temperature. This has been carefully studied recently by Rubenstein,[9] and by Harvey and Crockett.[10] The highest point in the curve comes a week or so before the onset of menstruation. There is an abrupt fall in the premenstrual period, and the lowest level is reached about ten to twelve days after the onset of menstruation corresponding to the preovulative phase. The range of variation is not great, perhaps 0.8 °C, but it may account for some of the higher temperatures found in women.

Emotion in certain susceptible individuals is a factor in raising body temperature, and may give high readings merely from the excitement of visiting the doctor's office. There have been reports of high temperatures in hysteria. In all such cases, however, there should be a suspicion of spurious readings, since these are not at all uncommon in neurotic young women, particularly those who have had nursing training. There are seven or eight different methods of obtaining false readings on a clinical thermometer and many physicians have been fooled for long periods of time.

Age is also a factor in body temperature. Premature infants have notoriously poor body control. They tend to resemble cold-blooded animals in assuming the temperature of the environment, and it is necessary to keep them in specially constructed bassinets or rooms with carefully controlled temperatures. Even normal infants show rather marked fluctuations in body temperature. Van der Bogert and Moravec[11] have recently made an excellent report on this subject. When they studied 717 school children they found, in the 7 to 8 year group, 43 per cent with oral temperatures over 37.2 °C (99 °F). This corresponds to a rectal temperature of about 37.8 °C (100 °F). In the 9 to 13 year old group, 33 per cent were above this level, but only 8 per cent of the children over 13. Old people seem to have about the same average temperature as young, but they are probably more susceptible to environment.

Many interesting studies have been made upon the temperature curves of normal individuals who have changed the day's routine and have worked at night. Results are conflicting, but it is evident that some individuals preserve the ordinary diurnal curve of lowest temperatures at 2 to 6 A.M. even though the night work is continued for a long time. Some show a tendency toward a flattening of the curve, others a complete reversal. Kleitman, in his recent book, "Sleep and Wakefulness,"[12] has reported many careful studies. He finds a slight fall in temperature when a man changes his position from standing to lying, and if a man lies down after standing for one hour the drop may amount to 0.2 °C. He also confirms the well-known drop in temperature when a person goes to sleep. He brings out the fact that the typical diurnal cycle of temperature first appears during the second year of the child's life, and he believes that learning to walk is the outstanding influence. Most interesting are the reports on his efforts to change the diurnal cycle by having normal men attempt to adopt, in their ordinary environments, days with cycles of 48 hours, or 12 hours, or 21 and 28 hours. In some the diurnal cycle was modified; in others it was scarcely changed at all. Dr. Kleitman and one of his associates lived for over a month in the Mammoth Cave and adopted a 28-hour day, 19 hours awake and nine in bed. One of the men changed his temperature cycle so that it corresponded to his 28-hour day; the other maintained the old 24-hour cycle. Kleitman believes that muscular activity is the chief factor in establishing the diurnal cycle. Once established, it seems to become a habit, stronger in some individuals than in others.

The mechanism of temperature regulation has been investigated for a long time, but it is only in recent years, and chiefly in this country, that quantitative studies of the various factors have been made possible. It was in America that the Atwater-Rosa-Benedict calorimeter developed into an instrument of precision for measuring heat loss. Vaporization from the surface of the human body was determined by weighing the water vapor. The calories of radiation and conduction were measured in a stream of cool water running through pipes at the top of the chamber in which the person was confined. For many years it was impossible to separate radiation from convection, but recently the development of radiometers by Hardy[13] and others has made it possible to calculate total radiation and thus find convection by difference. First it was necessary to determine the range of wave-lengths of heat loss from the human body. These all came between 4μ and 20μ with the peak at 9μ, all in the near infrared. At these wave-lengths Hardy confirmed the previous impression that the human skin came within one per cent of being a perfect blackbody radiator, and that the white man's skin was just as "black" as the negro's. The "blackness" of the skin made it easy to calculate radiation and skin temperature on the same instrument. In our calorimeter experiments we measure, every hour, the radiation and surface temperature at twenty different points on the body. The surface areas of each part of the body can be calculated from formulas worked out in the Russell Sage Institute of Pathology many years ago. The profile surface, which according to Lambert's law is the only one that applies to radiation, is taken as 75-85 per cent of the total surface, a result of many measurements. The radiation temperatures of the walls of the calorimeter are found by the same radiometer, and the total radiation from the surface of the body to the walls can therefore be determined. This method, with modifications, has been employed by Winslow, Herrington and Gagge[14] at New Haven in their brilliant studies of the effects of wide changes in environmental conditions. Our own experimental range in the Sage calorimeter is very limited, but illustrates many of the important fundamentals.

The calorimeter of the Atwater-Rosa-Benedict type is large enough for a man to rest comfortably for a period of three to five hours. The bed is made of woven fish line with a small folded sheet under the hips and back. Conduction is thus reduced to a minimum. In this calorimeter we studied in detail two normal men, 14 hours after the last meal, who lay naked and almost motionless at environmental temperatures between 22 and 35 °C. The results on one of them are shown in Fig. 6.[8] In the zone above 30 °C the skin was warm, only 2-3 °C below the rectal temperature. In the cold zone, around 23 °C (73 °F), the average temperature of the surface was 6.5 °C below the rectal temperature and the feet were almost as cold as the air. The toes were actually colder than the air. They are splendid radiators, usually moist with perspiration. They produce little heat in themselves and are far from the central heating apparatus.

It is obvious that there must always be a temperature gradient between the cool surface and the warm interior, and that in cold air the gradient goes deep.

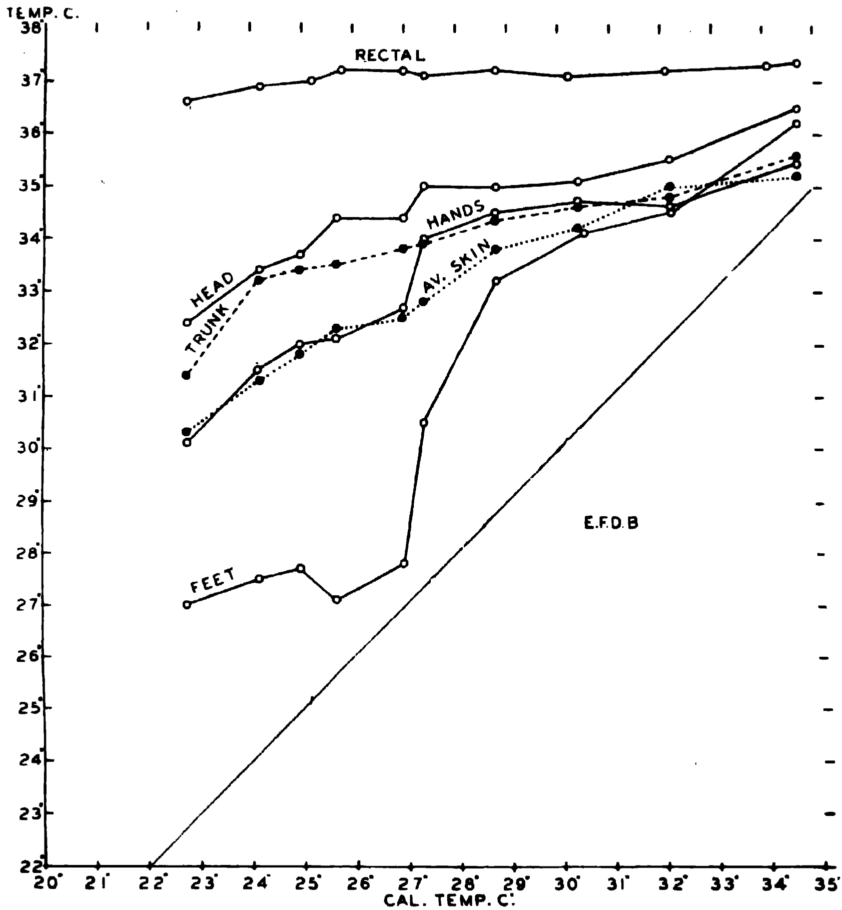

FIG. 6. Skin and rectal temperatures of normal control during basal experiments in calorimeter at different environmental temperatures. The dotted line shows the average skin temperature.

It is also obvious that the relatively constant rectal temperature gives only a partial indication of changes in the average body temperature. In 1915, Gephart and Du Bois[15] tried to work out the best method of calculating changes in average body temperature, but they used only a few surface thermometers of rather unsatisfactory design. They concluded that, although the changes in the surface temperature might give the best indication in typhoid fever, they were not on the whole as reliable as the rectal changes. Using better surface thermometers, Burton[16] in 1935 found the best agreement if he calculated average body temperature change by weighting the rectal reading 65 and the average surface temperature 35. In our own recent Sage calorimeter experiments we get the best results by weighting the rectal reading 80 and the average surface 20.

Heat produced in the muscles and organs of the body is dissipated at the surface by radiation, convection, and the vaporization of water. Each gram of water vaporized abstracts a little more than half a large calorie. The portion of heat loss through these channels is well shown by the results obtained on the two men studied in the Sage calorimeter (Fig. 7). Heat production remained very constant; heat loss in the cool experiments was much greater than heat production as the tissues near the surface became colder and colder. In this region it was radiation to the cold walls that accounted for the greater part of the loss, but the proportion fell to zero as the environmental temperature approached that of the skin. Convection played a minor role as the men were motionless in the bottom of the calorimeter where the ventilating currents were minimal. Vaporization accounted for only 18 to 20 per cent of the total in the cool zone, but increased by means of sweating to 100 per cent in the warm zone, where radiation and convection were necessarily abolished. In atmospheres between 28 and 30 °C, the so-called neutral zone, heat loss was nicely balanced with heat production by means of a delicate control of blood flow to the skin. Below 28 °C this blood flow diminished rapidly almost to zero and the skin was turned into a suit of clothes. Incidentally, it might be noted that the skin and subcutaneous fat are excellent insulators, just about as good as wool or cork.

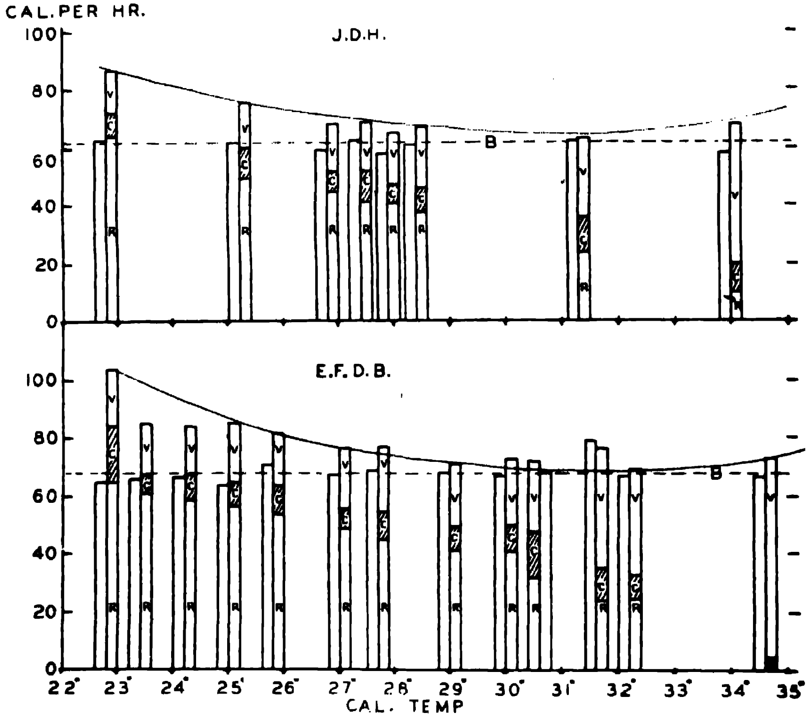

FIG. 7. Changes in heat production and heat elimination of two male subjects during the basal periods with increasing calorimeter temperatures. Blank columns on left, heat produced; columns on right, heat eliminated; V, vaporization; C, convection; R, radiation.

In temperatures above 30 °C the blood flow to the surface increased rapidly, accompanied by increased sweat. Vaporization is the safety mechanism for large increases in heat loss. At the cold end of the scale the safety mechanism expressed itself in chills, since the usual safety mechanism of voluntary muscular exercise was denied by the instructions to the subjects that they should attempt to remain motionless.

The human body evidently possesses a controlling mechanism similar to a good thermostat. There is a heat-regulating center contained in a few cells at the base of the brain in the region of the hypothalamus. If, however, this is destroyed or cut off from the rest of the central nervous system, temperature control is gradually reëstablished and there are secondary sites of control and even local control in the periphery of the body. Temperature regulation is too vital to be entrusted to any one small center in the brain.

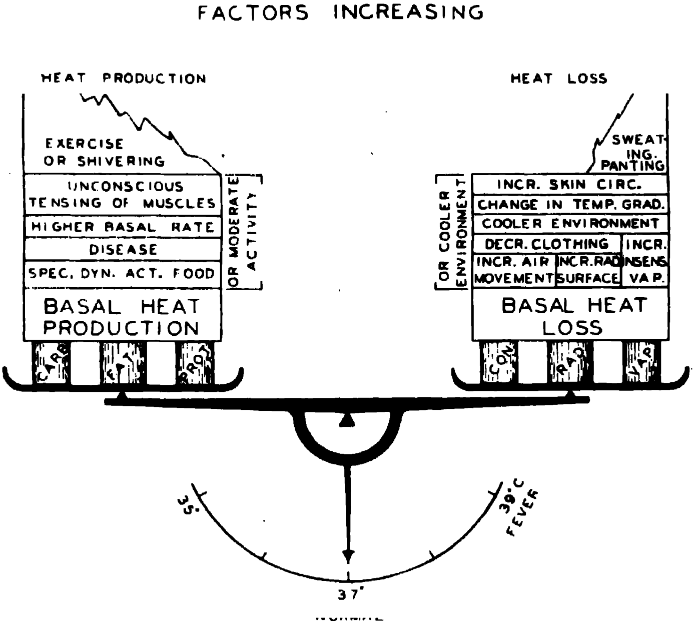

Fig. 8. Balance between factors increasing heat production and heat loss.

Unless there is extreme damage to the brain, the control of temperature is highly efficient. Sensory impulses are received by delicate cold and warm sense organs in the skin which can detect changes as small as 0.001 °C per second in three seconds. These impulses are carried to the spinal cord and brain. In the opposite direction, impulses from the brain and cord control the blood flow to various parts of the skin and to the sweat glands. The temperature center responds either to changes in the temperature of the blood stream or to changes in the temperature of the skin. It can institute conscious or unconscious adjustments in heat production as well as heat loss.

The balance mechanism is shown in Fig. 8.[17] On the left pan of the balance are the factors increasing heat production through the oxidation of carbohydrate, fat and protein; on the other pan the factors increasing heat loss through radiation, convection, and vaporization. Under basal conditions the loads are small and the balance is easily maintained. When the load on either side of the balance is increased, as, for example, by moderate activity on one side or by a cooler environment on the other, an adjustment is made on the opposite side. The great emergency mechanism in heat production is exercise or shivering; the one important factor on the other side is sweating, or, in the case of the dog, panting. The delicate adjustment of the body keeps the pointer close to 37 °C.

If heat production temporarily exceeds heat loss, the pointer swings toward fever levels. In fever itself, caused by infectious diseases, a new balance is established just as if the temperature-regulating mechanism were set at a different level. We might consider that the scale at the bottom of the diagram is shifted to the left so that, for example, the mark at 39 °C is now at the center of the curve and the balance reëstablished at this point. Plateaus of fairly level temperature are actually found in diseases such as lobar pneumonia, or the second week of typhoid fever, and the body establishes itself at this new level in much the same manner that it usually establishes itself at 37 °C. As a rule, however, most fevers show an irregular temperature with swings from 40 °C down below normal.

The exact cause of fever is not known. It can be produced, not only by disease, but also by a few drugs. Protein, foreign to the body, if introduced into the blood stream in very small amounts, will produce fever. For example, the usual dose of typhoid vaccine given to produce immunity consists of about one billion dead bacilli given subcutaneously. If 2 to 5 per cent of this dose is given into a vein, there will be, within 20 minutes to an hour, a sudden chill with a rise in body temperature, almost exactly similar to the chill that comes in malaria a short time after the moment when the malarial parasites break out of the red blood cells and scatter through the body. Apparently the presence of the foreign protein or malarial parasites acts on the temperature-regulating apparatus to set it suddenly at a higher level, say 40 °C. The body then finds itself three degrees too cold and proceeds to warm itself as rapidly as possible. Therefore, the emergency mechanism of chills is brought into play and heat production raised three- or fourfold. At the same time the skin usually becomes cooler and heat loss is kept either a little below or about the previous level. All the extra heat is stored in the body until the desired temperature is reached. Then the chill stops and the man is relatively comfortable. After a short time, in malaria, or after intravenous protein, the toxic effect on the heat center diminishes and it reverts to its normal regulating level. The body now finds itself about three degrees too warm and calls upon its emergency mechanism of sweating to reduce the temperature. This is shown in Fig. 9,[7, 17] which contrasts the results obtained in chills from cold atmosphere and chills resulting from malarial fever. In the first experiment, a normal man lay naked and motionless in an atmosphere of 23 °C (73 °F). This does not seem like very cold air, but it does feel cold when you have had no food since the night before and are lying motionless and naked. The rectal temperature fell slightly, but the average skin temperature dropped about three degrees centigrade and the man had a chill. Heat production rose from a level of 60 calories an hour to 140 calories per hour during the chill. The shivering and shaking increased convection, had no effect on vaporization, but actually diminished radiation since the skin was cooler. As a result of the storage of heat in the body, skin temperature rose more than a degree and rectal temperature rose slightly. After the chill, heat production dropped to its former level, skin temperature fell once more until another chill occurred just as the man was taken out of the calorimeter.

In the next experiment we had the man perform light work during the second and third periods of the observation. As his heat production rose, heat loss kept pace and the rectal temperature remained constant. Convection, however, increased with movement and the skin temperature fell a little. The third diagram was taken from an observation made on malarial chills in 1918,[18] with a line for skin temperature sketched in recently from observations made on other patients. Before

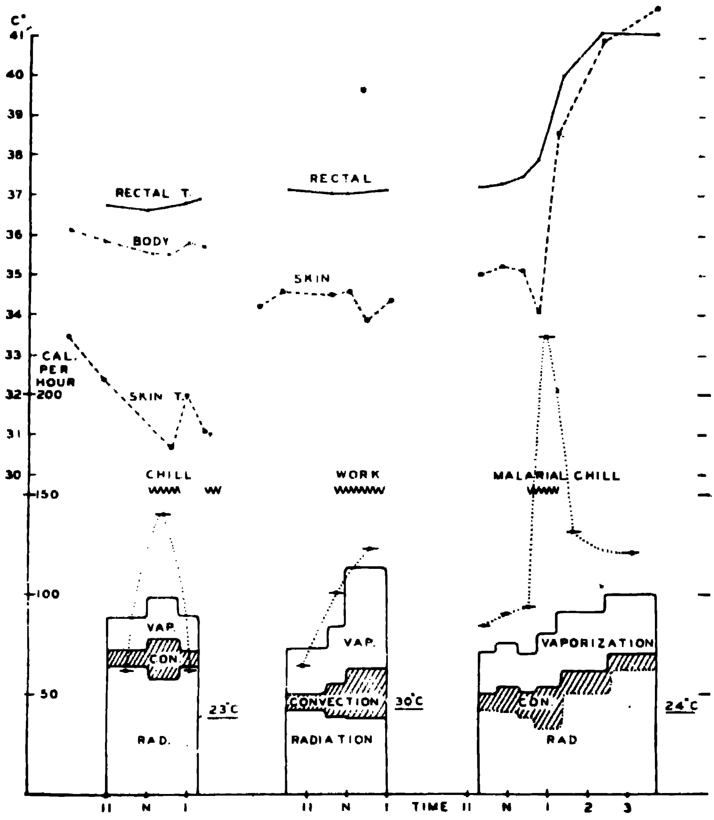

FIG. 9. Chills and muscular exercise. The first diagram shows chills which occurred spontaneously when the naked man was lying motionless in the calorimeter at a temperature of 23 °C. The dashed lines connected by dots show heat production, the columns heat loss.

The second diagram shows the effect of moderate exercise at a temperature of 30 °C.

The third diagram represents a malarial chill studied in 1918. There were no direct determinations of skin temperature or radiation but estimations have been supplied from later experiments.

the chill started, heat loss and heat production were approximately equal. During the thirty-five minute chill, heat production rose to the high level of 250 calories per hour, but heat loss was unchanged. This meant the storage of a large number of calories in the body with a sharp rise in rectal temperature to 41 °C. Soon after this peak was reached the man started sweating and his temperature fell to normal.

In most fevers the rise of temperature is less abrupt and there is no chill. Heat production is gradually increased; the heat loss either remains constant or diminishes. It may even rise slowly, but more slowly than heat production. There is in fever a marked tendency toward a warmer skin, whereas in the high temperatures produced by muscular exercise there is a cooler skin. Together with the fever there are, of course, many other physiological changes, such as the rapid pulse rate, rapid respiration, and the feeling of discomfort, due partly to the fever and partly to the toxic effect of the disease itself. There is an increase in the basal or resting metabolism roughly proportional to the degree of fever. In 1921[19] we plotted a curve showing the rise of metabolism in various fevers and found that it followed the van't Hoff law with about the same temperature coefficient as most chemical reactions.

At the present time we do not try to reduce fever unless the patient is very hot and uncomfortable, and then we use cooling sponges that cause a slight and temporary drop in the surface temperature. Antipyretic drugs have been almost entirely abandoned. The ice-water tubs used in typhoid fever thirty years ago have been discarded as useless and dangerous. Fever is perhaps beneficial in many ways as a defense against infection.

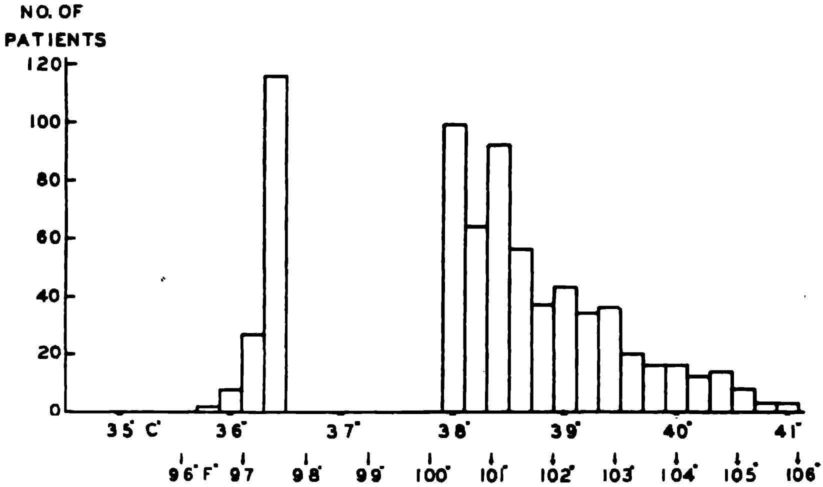

FIG. 10. Secondary regulation: Chart showing all temperatures of 38.0 °C or higher and 36.4 °C or lower found on 100 patients on the Medical Service, New York Hospital, 11/15/39. Secondary regulation for high temperatures occurs at about 40.5 °C and for low temperatures at about 36.5 °C.

In preparing this paper I found myself continually coming back to the question as to why the clinician finds so many patients with rectal temperature readings of 38, 39, and 40 °C, and so few over 41.0 °C (105.8 °F). This suggested that there was a secondary regulation of temperature at about the level of 41 °C which prevents temperatures from rising above this point, even in severe infections. I therefore studied all the charts on our four medical wards in which 100 beds were occupied by patients with various diseases, including a number with pulmonary tuberculosis, malaria, and a few contagious diseases. All the temperatures were rectal. In Fig. 10 are plotted the peaks of temperatures on every day when there was any reading above 38.0 °C, and also the lowest temperatures for all days when there was a reading of 36.4 °C, or lower. The result shows that in disease the limits of temperature are almost as sharply defined as in health, but of course the range is wider. There is a secondary wide zone of regulation with limits at about 40.5 °C at one extreme and at about 36.0 °C at the other. Within this wide zone there is a much finer regulation which keeps the temperature of normal people within about one-half a degree of 36.9 °C.

It must be remembered that these patients were all in a comfortable ward, most of them confined to bed. If they had been exposed to cold air, lower temperatures would have been found. Temperatures higher than 41.0 °C (105.8 °F) are relatively rare except in cases of heat stroke during very hot weather, or in men who work close to furnaces. Occasionally higher levels are encountered after intravenous injections of foreign proteins, or severe injury to the brain, or in patients during the hours just preceding death. Temperatures above 42 °C are dangerous since they approach the level at which body proteins are coagulated. The secondary regulation of body temperature, which resists a rise above 40.5 °C, is one of the most important defense mechanisms of the body.

In recent years there has been a great development in the method of fever therapy, since it has been found that certain organisms, particularly the gonococcus and the spirochete of syphilis, are killed by exposure to temperatures which can be tolerated for short periods by the human body. There are many methods of producing artificial fever, all of them quite evident if one studies the diagram showing the balance between heat production and heat loss. If a man is placed in a hot bath or if he is merely wrapped in a large number of blankets, his temperature will rise to 40 °C, but will rise rather uncomfortably. The method most commonly used consists in placing a man in a cabinet and warming the body by means of either radiant heat, high-frequency currents or electromagnetic induction. In some of the older cabinets the humidity was not raised and there was still considerable loss of heat through vaporization. Loss through vaporization can be diminished to zero by sufficiently high humidity. Now it is possible to bring the body temperature from normal to 41.5 °C (106.7 °F) in 50 to 80 minutes, and in certain cases it may be maintained at this level for 10 to 15 hours. That is exhausting and patients must be watched with extreme care. Most treatments are shorter than this. In some diseases the temperature is raised only as high as 40.5 °C and then brought down to normal in a few hours.

In general paresis, a late manifestation of syphilis, the usual treatment consists in inoculating with malaria and obtaining ten chills during which the temperature is maintained above 40 °C (104 °F) for a total of fifty hours. Sometimes temperatures of 40.5 to 41.0 °C are reached, but cold sponges are not given unless the temperature has been over 41 °C for thirty minutes. Sometimes typhoid vaccine is given intravenously instead of malaria. The results of malarial therapy are well established and it is now the regular method of treatment.

The most recent and dramatic application of temperature change in therapy is the cold treatment introduced by Fay and Smith.[20] They have obtained promising results in cancer by keeping the patients at extremely low temperatures, apparently without much discomfort. Even if this method should not prove to be of service in curing cancer, it is of enormous physiological interest in showing the possibilities of survival after extremely low body temperatures.

In this brief outline I have tried to present a picture of the human body as an apparatus which maintains a constant temperature under a large variety of environmental conditions. The fundamental principles of heat loss by radiation, convection, and vaporization should be of service to the air-conditioning engineers who are making life safer and more comfortable. There are many lessons to be learned from the consideration of the human body, and I doubt if there are any physicists, or chemists, or engineers who can suggest improvements in its construction or operation.

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Is Temperature a Basic Concept?*

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In physics texts temperature is ordinarily treated as a quantity which, like mass, length and time, is fundamental for problems and discussions involving heat. On the other hand, there are those who declare that temperature is just a convenient term for the average translational kinetic energy of a molecule of the body under consideration, or, as some prefer to state it, the energy per mole associated with the translatory motion of its molecules. Whether or not temperature or, for that matter, some other quantity in the field of heat involving temperature may be viewed in this or some similar manner and expressed in terms of the basic mechanical quantities mentioned, is the question under consideration here.

If the temperature of a body is merely a measure of the average translational kinetic energy of the molecules of the body, we should be able to write

$$T = k \cdot \tfrac{1}{2} m (v^2)_{\text{Av.}} \tag{1}$$

If we should select *on this basis* a temperature unit that would fit in consistently with other units of the cgs system, k would automatically become unity. Accordingly, we would say that, when the average translational kinetic energy of the molecules of a body is one erg per molecule, the body has a temperature of one erg. The temperature of some hydrogen, say, at the melting point of ice, thus expressed in ergs, would then be $5.66 \cdot 10^{-14}$ erg. Obviously the erg would be an inconveniently large unit of temperature, and one can understand why it would be desirable to take $2.07 \cdot 10^{-16}$ erg as one centigrade degree.

If physics were strictly classical, the foregoing identification of temperature with translational energy per molecule might reasonably stand. In the field of the classically ideal gas, the policy of identification does not give rise to difficulty. But gases, even ideal gases in the region of absolute zero where they become degenerate, are not classical; and liquids and solids are much more non-classical. Where quantum numbers are small, the distribution of energy among the molecules of a body is very different from the classical expectation.

Even at ordinary temperatures, when dealing with substances whose molal specific heats have not reached the Dulong and Petit limit of $3R$, one must conclude that the classical equipartition laws fail so far as the equilibrium between a solid and its vapor is concerned. The velocity distribution of the vaporized atoms of carbon, say, is not that of the surface layers of the solid carbon from which the evaporation has taken place. Though the solid and its vapor may be in temperature equilibrium, the average translational kinetic energy of the vapor atoms need not, and generally will not, be the same as the average translational kinetic energy of the atoms of the solid. (That some prefer to ascribe the internal energy of solids to stationary waves does not alter the situation.) Even in the cases of mixtures of such simple gases as helium and argon, when the temperature is so low that the energy is confined mainly to small quantum numbers, the average kinetic energies of the helium atoms will differ from the average for the argon atoms. On the concept that the temperature is a measure of the average kinetic energy of the molecules, the argon and the helium, though in equilibrium, would have different temperatures. Quantum considerations very strongly oppose the concept of a translational energy-temperature proportionality.

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* Reprinted from the *Am. J. Physics*, 8, 28, 1940, where it appeared under the title, "The Temperature Concept."

Our precise definition of a temperature scale is based on an application of the Carnot cycle proposed by Lord Kelvin. Where Q_0 and Q_1 represent, for a particular cycle, the quantities of heat absorbed and liberated, respectively, by the working substance used in the Carnot engine, this scale requires the corresponding temperatures T_0 and T_1 to be so related that

$$T_0/T_1 = Q_0/Q_1. \tag{2}$$

This scale is based on the assumption that energy is conserved in macroscopic processes, on the supposition that all possible p,v,T changes may be produced reversibly, and on the second law of thermodynamics. Developed in the days of classical mechanics, these basic assumptions and the temperature scale are equally applicable to the phenomena of the present-day quantum mechanics.

Direct experimental application of the Carnot equation in measuring temperature is impractical. With its aid, however, other usable relations have been developed, for example, that for the Joule-Kelvin effect,

$$\mu = 1/C_p[T(dv/dt)_p - v] \tag{3}$$

and the Boltzmann equation for blackbody radiation,

$$\mathcal{R} = \sigma T^4. \tag{4}$$

Using chiefly Equation (3), a precise temperature scale, ordinarily referred to as the *gas scale*, has been derived. It ranges from the gold point, 1336 °K, down to about 1 °K. There is great difficulty of application, however, near this lower limit. Above the gold point the radiation laws serve to carry the scale indefinitely upward.

Below the 1 °K-limit of the gas scale, workers make use of well-founded thermodynamic laws and of the approximate Curie law for paramagnetic substances, namely,

$$I = CH/T, \tag{5}$$

where I represents intensity of magnetization, H field strength, and C a constant. The results are probably trustworthy. It would be interesting, however, to determine experimentally whether or not the net transfer of heat between neighboring bodies in this temperature region would be in accord with those measured temperatures.

What is important here is that neither the gas scale nor the "low temperature magnetic scale" seems to include any quantity expressible in strictly mechanical terms, which is strictly proportional to temperature.

The Boltzmann fourth-power, blackbody law is highly exact. However, it applies only to the radiation contained in, or originating within, an opaque-walled evacuated cavity of uniform temperature throughout, whose dimensions are large in comparison with the wave-lengths of the contained radiation. Although experimental application of the law is quite impossible at very low temperatures, we may consider what, in theory, it suggests regarding the temperature concept. It seems perfectly possible (1) to bring in contact with any body whatsoever whose temperature is desired, another body shaped to form a cavity with opaque walls through which a small hole gives opportunity for observation of the blackbody interior, (2) to measure the radiancy $\mathcal{R}$ in watts per square centimeter, say, of the hole when the walls of the cavity have come into equilibrium with the body whose temperature is desired, and (3) to assign a temperature to the body in accord with the fourth-power law, that is, a temperature which would vary as the fourth root of the observed radiancy. For a case where the above-specified conditions are fulfilled, we should not hesitate, if convenient, so to assign a temperature, with the understanding that, except for experimental errors, such assignment could not be improved upon. Why not then identify the temperature of a body with the fourth root of the energy density within a contained, evacuated, opaque-walled enclosure? As in the case of the classically ideal gas considered earlier, there would be consistency. The natural cgs unit of temperature would then be the $(\text{erg/cm}^3)^{\frac{1}{4}}$, a temperature which we now rate at about 9350 °K. This unit would be inconveniently large, but a small part of it might be chosen as a unit for practical purposes.

Were all bodies provided with extended, opaque-walled, evacuated cavities with small holes for observation purposes, there would be no inconsistency in identifying the temperature of a body with the fourth root of the energy density in its appropriate cavity. However, there are difficulties. First, though not all bodies have such blackbody cavities, each possesses a radiant energy density which only in the rare case is equal to the energy density of a blackbody cavity in equilibrium. Secondly, in view of the huge dimensions demanded for reduced temperatures, the *sine-qua-non* condition of an opaque-walled cavity cannot always be fulfilled. Thirdly, liquids and gases cannot be shaped to give the desired cavities. Yet all solids and liquids and gases possess temperatures. It follows that the identification of temperature by means of the Boltzmann equation is not possible. Temperature is not just another name for radiant energy density or for the fourth root of such density.

Still another possibility needs consideration. In statistical mechanics, there occurs a parameter θ that has characteristics similar to those of temperature and is, in fact, identified with kT, k being the Boltzmann atomic constant. Given the total translational kinetic energy, the number of molecules and the type of statistics (Einstein's) applicable for an ideal gas, one may compute a value for θ. But the function used in the computation is very far from being a simple algebraic function of the fundamental quantities of mechanics. In addition, it involves a measure of the disorder of the system. What the function is for real gases, liquids and solids is quite uncertain, if indeed a universal function exists.

At present we know of no purely mechanical quantity—that is, one expressible in terms of mass, length and time only—which can be used, however inconveniently, in place of temperature. We are inclined to conclude that temperature is probably itself a basic concept.

The author is greatly indebted to his colleagues, Dr. E. Hutchisson and Dr. M. F. Manning for helpful considerations.

Discussion

Robert B. Sosman: Worthing presents here in a new aspect a philosophical question that has interested physicists since Clausius discovered entropy in 1865. The logical mind of the mathematical physicist resents having to base some of the most fundamental laws of physics upon a sensation—warmth versus coldness—in the skin of a man. He prefers that entropy and energy be taken as fundamental concepts, whereupon temperature becomes merely a secondary or derived quantity. The pragmatic philosopher, however, prefers to base his electromagnetics upon a piece of lodestone and a stroked cat; they can always be depended upon to produce the same experimental results even though one's notions of magnetic and electric fields have changed. Likewise, the temperature can always be tested with one's finger, even though ideas of what is meant by energy are hazy. See for instance, R. C. Tolman, "The Measurable Quantities of Physics," *Phys. Rev.*, **9**, 237-253 (1917), and P. W. Bridgman, "The Logic of Modern Physics," pp. 117-124, New York, 1928.

Gas Thermometer Scale Corrections Based on an Objective Correlation of Available Data for Hydrogen, Helium and Nitrogen*

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Established knowledge of the thermodynamic or Kelvin scale of temperature is intimately related to the known properties of gases† and to the concept of the ideal gas. The latter is, of course, an abstraction; but an increasing body of data, the product of a continuously improved technique in measurement, has established that at constant temperature every actual gas, as the limit of zero pressure is approached, exhibits a pressure-volume product which is rigorously constant.

It is equally well established empirically that the coefficients of pressure and volume increase of gases for the temperature interval ice—water and water—normal boiling point for many different chemically stable gases converge to a common value as the ice-point pressure approaches zero.

The thermodynamic temperature is in principle deducible from any thermodynamic formula based on the first and second principles of thermodynamics. A convenient formula to apply to gases is that for the Joule-Thomson coefficient; and experience shows that except for a unique temperature characteristic of each pure gas, the Joule-Thomson coefficient is finite and independent of the pressure as the pressure diminishes to zero. Expressed symbolically where μ is an abbreviation for the Joule-Thomson coefficient, H the enthalpy, v the volume of unit mass, C_p the heat capacity and τ the reciprocal of the thermodynamic temperature, we have the following equation

$$\mu = \left(\frac{dT}{dp}\right)_H = -\left(\frac{\partial v\tau}{\partial \tau}\right)_p \Big/ C_p = \mu_0 = f(\tau)_{p \to 0} \tag{1}$$

Integrating the latter equation between τ_0 and τ_{100} at constant pressure, there is obtained the following formula, where $\phi(\tau_{100}) - \phi(\tau_0)$ is the value of $\int C_p^0 f(\tau)\,d\tau$:

$$[v_{100}\,\tau_{100} - v_0\,\tau_0 = \phi(\tau_{100}) - \phi(\tau_0)]_{p_0} \tag{2}$$

From this equation we may easily form the conventional coefficient for volume increase at constant ice-point pressure, p_0. The result is as follows where α_p designates the average expansion coefficient over the range 0 °C to 100 °C.

$$\frac{v_{100} - v_0}{v_0 100} = \frac{1}{T_0} + \frac{T_{100}}{100}\Big[\phi(\tau_{100}) - \phi(\tau_0)\Big]\frac{1}{v_0} \tag{3}$$

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* (Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 436.)

† At temperatures below 10 °K and especially below 1 °K it is practical to use a paramagnetic salt as a means of realizing Kelvin Scale temperatures. In this case exact magnetic susceptibility and heat capacity data are required. The present paper is concerned with temperatures which can be measured with a gas thermometer, namely from about 2 °K as the lowest practical limit.

Now it follows that in the last equation as the volume at 0 °C, v_0 becomes progressively larger, the value of α_p tends increasingly to the value T_0^{-1}. In consequence we are led to conclude that the empirical finding of the convergence of the volume coefficients to a common value for different substances supplies a measure of the value of the reciprocal thermodynamic temperature of the ice point.

Another important thermodynamic formula related to the theory of the temperature scale is the following, where U is the energy per unit mass.

$$\left(\frac{\partial U}{\partial v}\right)_T = -\left(\frac{\partial p\tau}{\partial \tau}\right)_v \tag{4}$$

Unfortunately the quantity λ is extremely difficult to measure accurately, owing to its small value and the adsorptive properties of gases.[1] The meager experimental results indicate however, and J. R. Roebuck's calculations confirm the fact, that λ varies inversely as the product of the inverse square of the volume and a temperature function. Expressed symbolically we have the relationship:

$$\lambda = \frac{g(\tau)}{} \tag{5}$$

It follows, therefore, that λ approaches zero rapidly as v increases. On integration we arrive at the equation following:

$$(p\tau)_{100} - (p\tau) \quad \frac{1}{v_0^2}\left[F(\tau_{100}) - F(\tau_0)\right] \tag{6}$$

Designating the pressure expansion coefficient by the symbol α_v, we find the relation:

$$\frac{p_{100} - p_0}{p_0\,100} = \alpha_v = \frac{1}{T_0} + \frac{T_{100}}{100 v_0^2}\left[F(\tau_{100}) - F(\tau_0)\right]\frac{1}{p_0} \tag{7}$$

Here, as in the case of the volume coefficient, α_v tends to T_0^{-1} as the volume increases to infinity, and the convergence of the α_v values to a common value again supplies the means of locating the thermodynamic temperature of melting ice.

It is seen that λ is zero unconditionally as infinite volume or zero pressure is reached, but that μ_0, according to present experience, remains in general finite except for a unique temperature (inversion point). The quantity μ_0 may also tend to zero as very high temperatures are approached, assuming chemical stability of the gas at elevated temperatures. Reasons for supposing such a condition possible will be presented later; but the temperatures of experiment, except in the case of helium, give little indication about the behavior of $f(\tau)$ at very high temperatures. In addition to Joule-Thomson data there exists, of course, a large body of pressure-volume-temperature data for the acceptable thermometric gases from which μ_0 and λ or their equivalents may be computed.

At low pressures we may write $\left(\frac{\partial p_T}{\partial \tau}\right)_{v,m} = 0$, which leads directly to the result following:

$$(p = f(v)T)_m \tag{8}$$

It has been seen, however, that the pressure-volume product for vanishing pressures is constant at constant temperatures. We conclude then that $vf(v)$ is a constant for every gas, and Equation (8) may be written

$$pv = vf(v)T = (\text{constant} \times T)_{p\to 0} \tag{9}$$

The experimental data on the chemical combinations of reacting gases lead to the conclusion that equal volumes of all gases, temperature and pressure being taken the same, contain the same number of molecules or particles, *i.e.*, Avogadro's principle. It therefore follows that, if the unit of mass is chosen equal or proportional to the molecular or particle weight, the constant in Equation (9) is universal.*

The foregoing résumé includes all the facts pertaining to pure gases needed to realize empirically the thermodynamic scale of temperatures. From the practical point of view, however, two alternatives present themselves, as follows. First, we may carry out observations of the gas-scale temperatures at various ice-point pressures at fixed temperatures maintained by reliable secondary indicating thermometers. The thermodynamic temperature will then be the gas thermometer reading which results from extrapolation of the successive readings to zero pressure. Secondly, we may carry out Joule-Thomson measurements or utilize p,v,T data for the thermometric gas and compute corrections to the readings of the gas thermometer for each ice-point pressure. Starting, for example, with Equation (2) and the definition of temperature on the gas scale, $\left[\frac{v_t - v_0}{v_0\alpha_p}\right]_{p_0} = t_g$, we find the following equation expressing the difference between the gas temperature and the thermodynamic temperature t:

$$- t_g = \frac{T}{v_0\alpha_p}\left(\phi(\tau_0) - \phi(\tau)\right) + t\left(\frac{\alpha_p - \alpha_0}{\alpha_p}\right) \tag{10}$$

Here $\alpha_p \rightarrow \alpha_0$ for $p \rightarrow 0$ or $v_0 \rightarrow \infty$ whence $t_g = t$.

Corrections for the almost universally used constant volume scale can be sought in terms of λ, but unfortunately as stated above no directly measured values are available. In view of this the most direct procedure appears to be use of the Joule-Thomson data to establish the low-pressure equation of state of the gas.

The Low-pressure Equation of State

Returning once more to the special equation (1), its general integral may be written as follows:

$$v = \Psi(p)T + T\int_0^\tau f(\tau)C_p^0 d\tau \tag{11}$$

Here the $f(\tau)$ and C_p^0 of the integrand are pure temperature functions for $p \rightarrow 0$, the former by direct experiment, the latter from the known heat capacity properties of gases under pressure. In carrying out the integration, the limits of integration are important and will be considered later. The quantity $\Psi(p)$ on the basis of our knowledge of the properties of gases at low pressures may be set equal to R/p. As a general result it is therefore seen that if the second term of the right-hand member of (11), a pure temperature function, is set equal to B_0, we may write the equation of state as follows:

$$p = \frac{RT}{v - B_0} \tag{12}$$

Of course B_0 may be, and usually is, evaluated directly from p,v,T data by extrapolating $(v - RT/p)$ to zero pressures. The value of λ, however, may now be found as follows:

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* The foregoing résumé is really a recital of the interrelations of existing empirical knowledge about the properties of pure gases leading to our belief in the existence of the ideal gas state realizable through reduction of the pressure. For a treatment proceeding along different lines and applicable to both pure gases and mixtures, the following paper should be cited: J. A. Beattie, *Phys. Rev.*, 36, 132 (1930).

$$-\left(\frac{\partial p\tau}{\partial \tau}\right)_v = \lambda = -\frac{R}{(v - B_0)^2}\frac{\partial B_0}{\partial \tau} = -\frac{R}{v^2}\frac{\partial B_0}{\partial \tau} \tag{13}$$

From the last equation * the scale corrections can be readily deduced, resulting in the equation:

$$t_a = \frac{RT(B_0{}^0 - B_0{}^t)}{v_0{}^2 p_0 \alpha_v} + t\left(\frac{\alpha_v - \alpha_0}{\alpha_v}\right) \tag{14}$$

Considerable insight into the relationships above, and help in the correlation of data, result from indications about the low-pressure equation of state following from the application of statistical mechanics. The equation of state may be derived in the form of Equation (12), where B_0 is a pure temperature function given in the simplest case (exclusive of quantum effects) by the formula:

$$B_0 = 2\pi N \int (1 - e^{-\beta w}) r^2 dr \tag{15}$$

where $\beta = (kT)^{-1}$, k being the gas constant per particle, and w the intramolecular potential between a pair of particles. For the van der Waals concept of the molecular field (perfectly reflecting spheres on contact, otherwise a spherically symmetrical attractive potential) $B_0 = b - \frac{a}{RT}\left(1 + \alpha_1 \frac{a}{RTb} + \ldots\ldots\right)$.† The more general concept expressed by the equation $w = \gamma_1 r^{-n} - \gamma_2 r^{-m}$ leads to the expression

$$B_0 = \beta_0 \tau^{3/n} - A_0 \tau^{\frac{3+n-m}{n}} - A_1 \tau^{\frac{3+2(n-m)}{n}} - \ldots\ldots\ldots \tag{16}$$

Other expressions for w may be assumed, but a restricted number lead to known functions when used to solve the integral of Equation (15). It is, however, possible to express the potential as follows:

$$w = \frac{\gamma_1}{r^n}\left(1 + \frac{\alpha_1}{r^2} + \frac{\alpha_2}{r^4} \ldots\right) - \frac{\gamma_2}{r^m}\left(1 + \frac{\beta_1}{r^2} + \frac{\beta_2}{r^4} \ldots\right) \tag{17}$$

This leads to an integral similar in form to (16), wherein the terms written are repeated with the addition of cross terms arising from the expansion and evaluation of the integral.

At low temperatures quantum effects become important for the gases helium and hydrogen, but an exact calculation of B_0 requires a very precise knowledge

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* The quantity λ may also be written in terms of μ, the Joule-Thomson coefficient, thus,

$$\lambda = -\left(\frac{\partial p}{\partial v}\right)_T\left[\mu C_p + \left(\frac{\partial(pv)}{\partial p}\right)_T\right]$$

Using the available p,v,T data and Joule-Thomson coefficients, λ has been computed by J. R. Roebuck using this equation. By the method outlined above, λ_0 may be computed from μ_0 data alone. It is regrettable that the problem of measuring λ directly has not been solved.

† The attractive potential varies as r^{-6}, an approximation justified by the quantum mechanical theory of the intramolecular potential. This gives

$$B_0 = b - \frac{a}{RT}\sum_{j=0}^{\infty}\frac{1}{j!(2j-1)!}\left(\frac{a}{RTb}\right)^{j-1}$$

of the potential function w. A definite computation of the B_0 values at low temperatures where quantum effects are significant has in consequence not been completed. It is therefore necessary for the present to utilize the combined resources of existing empirical and theoretical knowledge to secure as exact a temperature formulation of the existing B_0 and $C_{p0}\mu_0$ data as possible. Such a formulation will supply the means of reducing all gas-thermometric scale readings to the thermodynamic scale and at the same time furnish evidence regarding the probable degree of reliability of the temperature scale.

Semi-empirical Formulation of p,v,T Data for Hydrogen, Helium and Nitrogen

The quantity desired for the present purpose is the value of B_0, the so-called second virial coefficient. To obtain the quantity from p,v,T data requires, as stated, extrapolation, in principle, of the function (or its equivalent) $(v - RT/p)$ to the zero of pressure or density. The unfavorable aspect of the matter is that even at appreciable pressures, 10 atm. for nitrogen, the difference in v and RT is only a part in 230 at 0 °C. For helium at 0°, similarly, the difference is a part in 190, and in the case of hydrogen it is a part in 163. When consideration is given to the disturbing effects of adsorption together with the difficulties of precise control of the volume of the container as a function of the tension and temperature, the large variability of the B_0 values deduced from the data of independent observers can be easily comprehended.

The usefulness for many theoretical as well as practical problems of highly exact B_0 values for substances is very great. What is required to supply the need is a method of measuring B_0 directly. The most promising method at the moment appears to lie in the measurement of the change of the enthalpy with pressure for various constant temperatures at low pressures. In those cases where full knowledge of the heat capacity is available, as is the case for the thermometric gases, the values of μ_0 supply the equivalent values, *i.e.*, $(\mu_0 C_{p0})$.[3] The results already obtained with steam, hydrogen, and nitrogen encourage the belief that the remaining experimental difficulties can be ultimately surmounted and values in the range 500 °C to low temperatures can be obtained.

At the present time a large temperature range of μ_0 values for two of the thermometric gases is available, in addition to considerable B_0 data from p,v,T measurements. An attempt has therefore been made to treat all existing data in an objective manner with the expectation of obtaining "most probable" B_0 values, The need for the effort is considerable because of expanding research at low temperatures where uncertainty approaching nearly one per cent in the Kelvin temperature at 4° may exist. At higher temperatures (0 to 500°) my colleagues, J. A. Beattie, B. E. Blaisdell and J. Kaye, have found significant differences between the International Scale (1927) and the Thermodynamic Scale through their nitrogen gas-thermometric measurements. From their results and the present calculations it is inferred that the accepted value for the Kelvin temperature of melting gold may be in error to a considerable extent. For the nitrogen thermometer a high precision in the B_0 values is required, because the quantity $(t - t_{gas})$ appears as the difference between two terms about tenfold larger than $(t - t_g)$ at 400 °C.

It is fortunate that we now have available the data of J. R. Roebuck and H. Osterberg on the values of μ_0 from their painstaking measurements of the Joule-Thomson temperature effects for nitrogen and helium over extended temperature ranges. In the case of helium the low-pressure heat capacity $C_p{}^0$ is independent of both pressure and temperature, whereas in the case of nitrogen the C_p^0 values deduced from spectroscopic values are now definitive. By combining these data in the product $\mu_0 C_p^0$ we arrive at values equivalent to $\frac{\partial B_0\tau}{\partial\tau}$ from which B_0 values may be obtained.

The least square method of correlation has been used in principle, but it was long ago observed by the author in earlier unreported correlative experiences with the class of data under consideration that a routine application of statistical methods does not always lead to the most satisfactory correlation. The basis of this somewhat startling statement relates to the generally admitted observation that there are varieties of data obtainable under the conditions exemplified in the present B_0 data which involve unknown constant errors. Such ensembles of data are not favorable for the simplest mode of treatment by standard statistical methods. The problem here attempted would of course be greatly simplified if the functional relationship between the B_0 values and the temperature were exactly known for the gases of interest. Theory in the present case would settle the matter, provided means were available for establishing the intermolecular potential required for computing B_0.* [4] In the circumstances, therefore, the final correlation is the result of bringing to the solution of the problem some considerably earlier experience, while using all the resources of theory available.

The final formulas adopted for B_0 all have one characteristic in common: they require that B_0 become zero for $\tau = 0$, as well as for a finite temperature (Boyle point). This quality is of great convenience, for in evaluating the integral $d(B_0\tau)$ the result becomes simply $B_0\tau$, and the relation between the $(\mu_0 C_p^0)$ values and B_0 values is simple. The assumption may be taken to mean that $w = f(r)$; the intramolecular potential becomes finite rather than infinite for $r = 0$, assuming of course that the particles do not lose identity as they are pressed into one another. The integrand in (15) contains the factor $(1 - e^{-\beta w})$, a quantity which becomes 0 or +1 as βw goes to 0 or to $+\infty$. βw is, however, proportional to the energy of interaction of a particle pair divided by the thermodynamic temperature. Consequently, if the rate of increase of w with falling r is retarded sufficiently for small values of r, the quantity βw would become effectively zero for $\tau = 0$.

A form of w already mentioned in connection with Equation (16) is convenient because the integral (15) can be evaluated by the gamma function theorem [5] where n is an integer taken to be of the order 9 to 14. As already stated, B_0 for this form of w becomes $B_0 = \beta_0\tau^{3/n} - A_0\tau^{\quad n}$ .... Adopting such a general type of formula on an essentially empirical basis, it is convenient to form the quantity $B_0T^{3/n}$, using observed values of B_0 and T, plotted in relation to various powers of τ. In the case of helium, for example, it is found that an essentially linear relation is obtained from the highest temperatures (400°) to about −100° if $B_0T^{1/4}$ is used with $\tau^{1/2}$ as abscissae. The use of either of the "n" integers 11, 13, 14, appears not to make enough difference to forego the conveniences of using 12; and for all three gases $B_0T^{1/4}$ was finally adopted for the first term of $B_0 = f(\tau)$. For helium and hydrogen the entire range of the existing data has been represented by the form following:

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* I. Amdur at M.I.T. has been able to control a neutral atomic hydrogen and helium beam and measure the scattering in neutral gases for fixed angles. The observed data lead directly to values for w.

$$B_0T^{1/4} = \beta_0 - A_0\tau^{1/2} - A_1\tau \ldots\ldots\ldots \tag{18}$$

In the case of nitrogen, however, the smallest average deviation between alternative analytical representations and observed B_0's over the range 400 − 150 °C was obtained using the form

$$B_0T^{1/4} = \beta_0 - A_0\tau^{3/4} - A_1\tau^{15/4} \tag{19}$$

These forms will perhaps ultimately prove too simple in view of the long temperature range covered, but it appears unprofitable at present to expend a longer time seeking other forms until data of greater precision and consistency become available.

A copious array of B_0 values exist for helium. The values of B_0 (400 to −258 °C) obtained by the investigators of the Charlottenburg laboratory have been listed and discussed by F. Henning in his 1928 paper[6] on scale corrections. The Leiden Laboratory data represent the efforts of many investigators over a long period of time and range from 373 °K to a few degrees above 0 °K. In addition we have the B_0 results from the work at the Fixed Nitrogen Research Laboratory at Washington, D. C.,[7] and finally the μ values from the measurements of J. R. Roebuck and H. Osterberg.[8]

For hydrogen the bulk of the available data is from the Charlottenburg and the Leiden groups. The older Amagat data was not included in the correlation effort because exact low-pressure (under 100 atm.) data are the most suitable for obtaining B_0 values. Similarly Bartlett's excellent nitrogen data at high pressures were not used. Having secured B_0 values, however, higher density data become invaluable for deducing the third and higher order verial coefficients.

Plotting the values of $B_0T^{1/4}$ with τ^s, where s is chosen to give a linear relationship at the higher temperatures, values of β_0 were finally obtained by least square computation, using the data of the principal laboratory groups. This was necessary since the data of the principal laboratories give B_0's differing in trend, particularly in the case of helium. The several values of β_0 were then averaged without weighting. The average value was next used to form the function following:

$$\omega = (\beta_0 - B_0T^{1/4})T^s \tag{20}$$

The value of s for hydrogen and helium was 1/2 and for nitrogen 3/4. The next step was to plot ω with τ^t in the attempt to locate a value t which would yield a linear relationship with the ω's. For helium and nitrogen t appears to be 1/2 and 3 respectively.

Hydrogen

In the case of hydrogen the ω's are linear in $\tau^{1/2}$ to the normal boiling point, about 20 °K. The data of van Agt and Onnes below 20 °K (4 points) and Onnes and de Haas (1 point) indicate larger values (Fig. 1 *) of ω than the higher temperature linear relation would suggest. The attempts to include these data in a correlative equation will not be reported because of a lack of corroborating experimental values of B_0 below 20 °K.

A least square treatment of all the ω data to the normal boiling point of hydrogen was made, including all available data except the Nijhoff and Keesom †

* The ω value due to Onnes and de Haas is exceptionally large relative to the van Agt and Onnes points. One at −257.1 lies off the figure and also one at −257.1 due to van Agt and Onnes.

† The five entries in Table I of Suppl. 64 C are evidently tenfold too small.

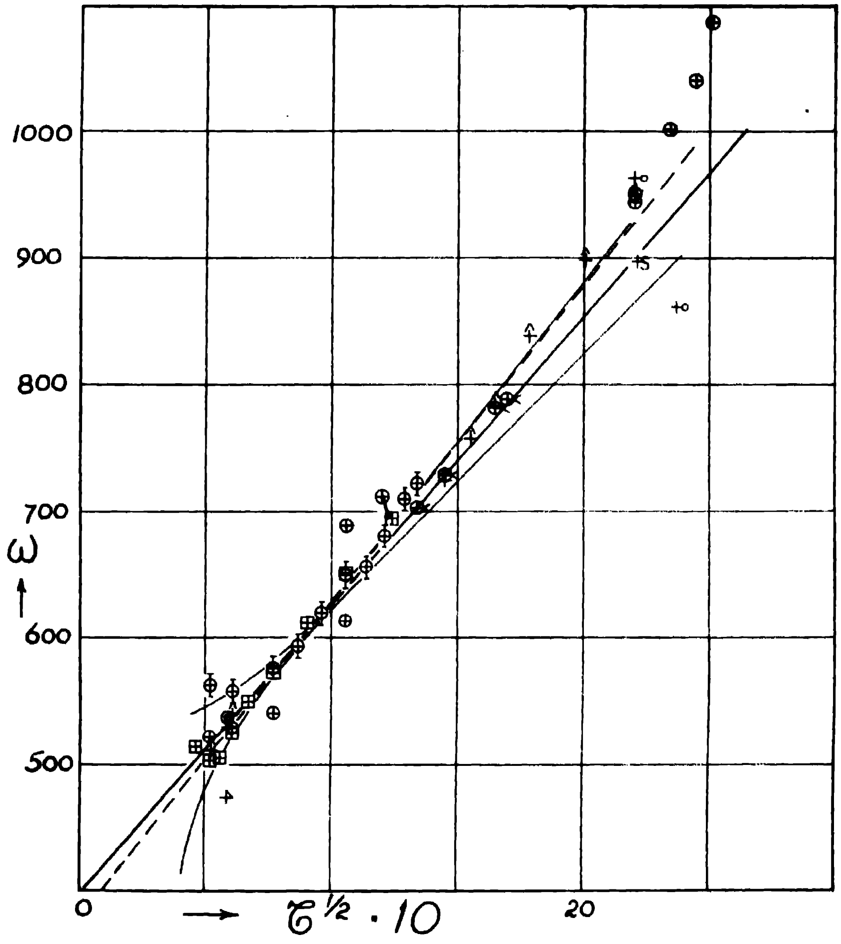

Fig. 1. Hydrogen Plot.

The ordinates ω are the same in kind as used for Fig. 2. Φ Onnes and Braak; ⊕ Witkowski; ✢ Onnes, Crommelin and Smid; +S Schalkwijk; ✢ Palacios, Martinez and Onnes; +∘ Onnes and de Haas; ⊞ Holborn, Holborn and Otto; ⊕ van Agt and Onnes; ⊕ Crommelin and Swallow; ⊕ Verschoyle; † Nijhoff and Keesom. To avoid congestion, values of $B_0(\omega)$ due to Gibby, Tanner and Masson; Tanner and Masson; Otto; Michels, Nijhoff and Gerver; Witkowski; Wroblewski; Onnes and Penning have not been entered. The full straight line represents Equation (21A) of the text; the dotted line, Equation (21B). The lines on either side of (21A) represent the values of ω due to a plus and minus five per cent change in the computed ω.

and the van Agt and Onnes data below the ice point and below about 20 °K respectively. The equation for $B_0T^{1/2}$ follows:

$$B_0T^{1/2}\frac{\text{cc.}}{\text{g.}} = (60.000 - 397.25\tau^{1/2} - 2282.056\tau) \text{ hydrogen} \qquad (21A)$$

The inclusion, however, of all the Nijhoff and Onnes data,‡ but rejecting the

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‡ After multiplying the low-temperature values given in Suppl. 64 C by 10

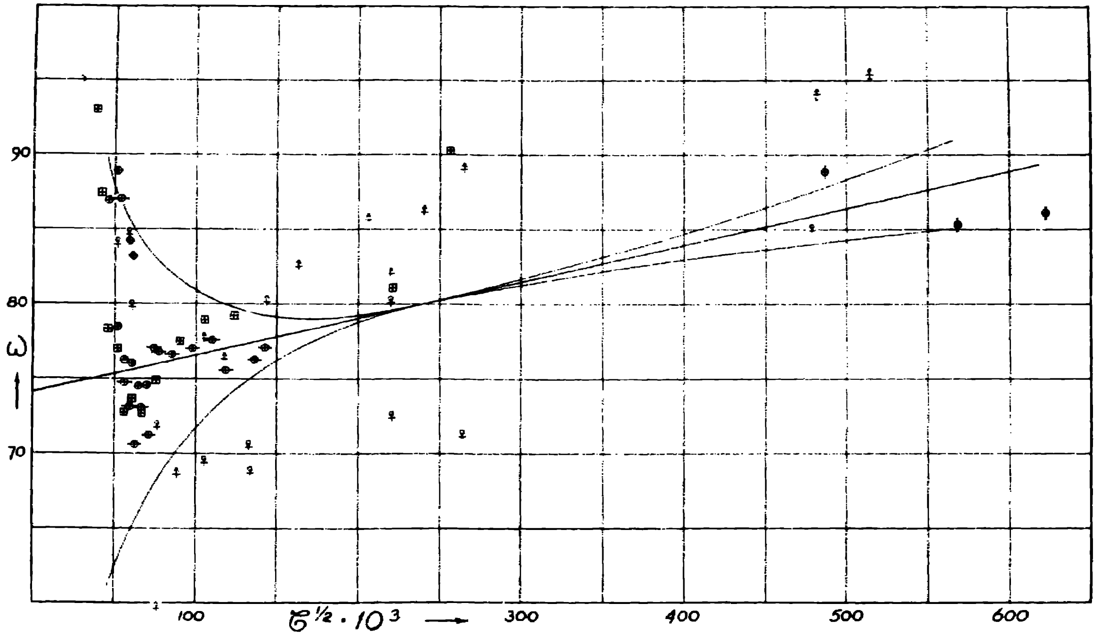
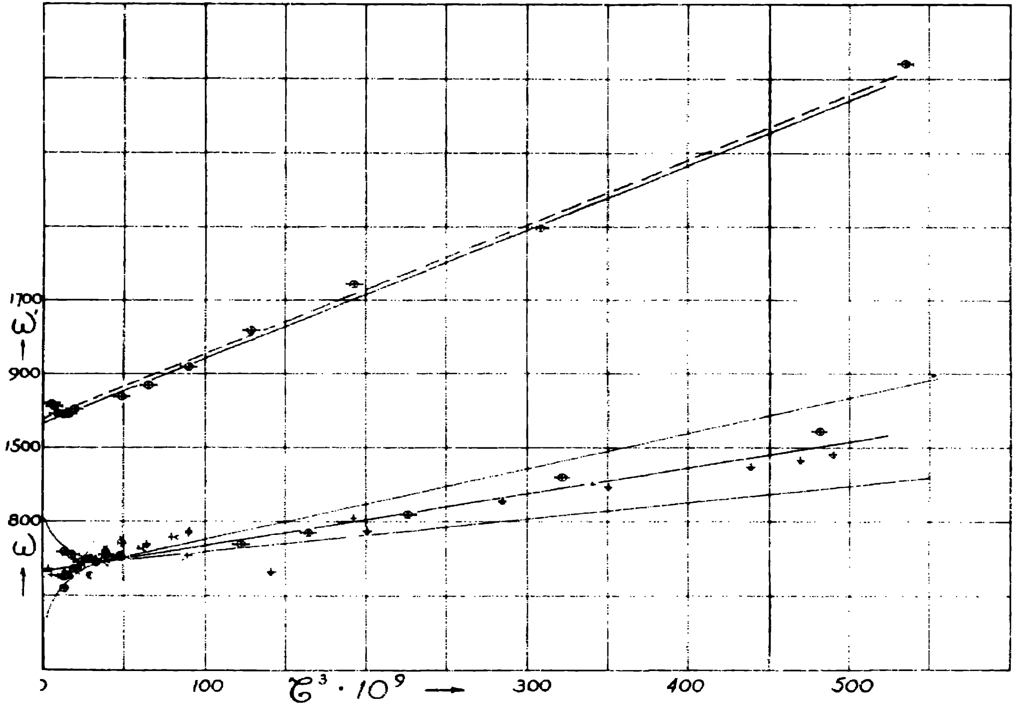


FIG. 2. Helium Plot.

As ordinates the quantity $(16.4873 - B_0T^{1/4})T^{1/2}$ (represented by ω) is entered with $\tau^{1/2}.10^3$ as abscissae. The quantity $(5/4 \times 16.4873 - \Psi_0T^{1/4})T^{1/2}.4/7$ is also entered with $9/7\ \tau^{1/2}.10^3$) as abscissae. Here B_0 is the second virial coefficient in cc/g, while ψ_0 is $\mu_0C_{p_0}$ in cc atm energy units per atm. It was impractical to place every datum in the chart. ϕ Keesom and Braak; ⊕ Keesom and van Santen; ✝ Keesom and Onnes; ‡ Onnes and Boks, (corrected by van Itterbeck); † Nijhoff, Keesom and Iliin; ⊞ Holborn and Otto; ⊕ Wiebe, Gaddy and Heins; -⊕- Roebuck and Osterberg. B_0 values due to Tanner and Masson; Gibby, Tanner and Masson; Otto, van Agt and Onnes; Palacios and Onnes; Penning and Onnes; and Onnes have not been entered. The straight line represents Equation (22) of the text; the lines on either side correspond to a plus and minus five per cent deviation in the B_0 values computed by Equation (22).



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In the lower portion ordina are values of ω or 0.0(− $B_{(}T^{1/4})T^{3/4}$ and 1/2(5/4B_0 − $\Psi_0{}^{(T^{1/4})}T^{3/4}$ wi h τ^3.10⁹ and (5/2τ^3.10 a: the abscissae. In the upper half twice the second of the foregoing o linates due to Roebuck n Osterberg's c ta are plotted with τ 10⁹ as abscissae. The two right-hand points o the upper half of the figur are omitted in the lo portion. + F ysikalische Reichsan alt data: Henning and Heuse, Holborn and)tto; ⊕ On es and van U , Roebuck and)s berg; ⊕ Versc oyle: ● Michels, Wouters and de Boer; ◐ Otto, Michels and Wouters; +C Collins and Keyes. Data due to Keyes, S ith and Taylor,)tto, and Chappuis h ve not been entered. The dotted line in the upper portion of the figure epresents the least s re correlation of Roebuck and Osterbe 's results only, or Equation (25B); the full line Equation (25A). The lines on either side he straight lin in the lower half of he figure represent the values of ω for plus and minus five per cent chang in th B_0 values corr ed by means of Equation (25A).

points at −255.32 °C due to Onnes and de Haas and those of van Agt and Onnes at −252.54 °C and below, leads to the equation:

$$B_0 T^{1/4} \frac{\text{cc.}}{\text{g.}} = (60.000 - 380.56\tau^{1/2} - 2494.8\tau)\ \text{hydrogen} \tag{21B}$$

For temperatures below −100 the latter formula is likely to be more satisfactory, but above −100 to 150 °C the differences in B_0 values computed from either formula seem satisfactory relative to the degree of precision in the observational material. The corrections to the one meter ice-point pressure constant-volume hydrogen gas thermometer scale are computed from formula (21B). The graph, Fig. 1, shows the relation of ω to $\tau^{1/2}$.*

Helium

The data for the helium B_0 values as already stated are represented by a formula similar to that employed for hydrogen. The least square treatment of the B_0 data led to an equation with somewhat different constants from that deduced from the $\mu_0 C_p{}^0$ data of Roebuck. The following equation adopted was formed by averaging the constants for the two groups of data.

$$B_0 T^{1/4} \frac{\text{cc.}}{\text{g.}} = (16.4873 - 74.09\tau^{1/2} - 24.6\tau)\ \text{helium} \tag{22}$$

The graph, Fig. 2, shows the $\omega : \tau^{1/2}$ relationship. In order to include the data of Roebuck and Osterberg on the same plot, use was made of the following relationship:

$$\mu_0\, C_p{}^0 = -\left(\frac{\partial v\tau}{\partial \tau}\right)_{p\to 0} = -\left(\frac{\partial B_0\tau}{\partial \tau}\right) = \Psi_0 = 5/4\beta_0\tau^{1/4} - 7/4A_0\tau^{3/4} - 9/4A_1\tau^{5/4} \tag{23}$$

making use of the above form for B_0. It is, however, evident that the last equation may be written:

$$\left(\frac{5}{4}\beta_0 - \Psi_0 T^{1/4}\right) \times \frac{4}{7}\, T^{1/2} = A_0 + A_1\left(\frac{9}{7}\tau^{1/2}\right) \tag{24}$$

The values of the left-hand member were accordingly entered with the ω values derived from the B_0 values but with ordinates of value $(9/7\tau^{1/2})$.

Nitrogen

The treatment in the case of nitrogen follows the same pattern as for hydrogen and helium. In Fig. 3, however, the upper half represents the value of $\left(\frac{5}{4}\beta_0 - \Psi_0 T^{1/4}\right) T^{3/4}$ versus τ^3 as abscissae from the data of Roebuck and Osterberg.[9] In the lower half of the Fig. 3, the $\frac{1}{2}\left(\frac{5}{4}\beta_0 - \Psi_0 T^{1/4}\right) T^{3/4}$ quantities from Roebuck and Osterberg were entered as ordinates together with $\left(\frac{5}{2}\tau^3\right) \cdot 10^9$ as abscissae, excepting however the points for the two lowest temperatures, which could not be entered without unduly lengthening the figure. The following equation was obtained by averaging the constants of the independently correlated Ψ_0 and B_0 data.

$$B_0 T^{1/4} \frac{\text{cc.}}{\text{g.}} = (10.08 - 766.115\tau^{3/4} - 1.7545 \cdot 10^8\tau^{15/4})\ \text{Nitrogen} \tag{25A}$$

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* The full line is represented by Equation (21A), the dotted one by (21B).

The equation based on Roebuck and Osterberg's results alone follows:

$$B_0T^{1/4}\frac{\text{cc.}}{\text{g.}} = (10.08 - 767.33\tau^{3/4} - 1.812\cdot 10^{8}\tau^{15/4})\text{ R. and O. Nitrogen} \qquad (25B)$$

Gas Scale Corrections

Tables 1, 2, and 3 contain the scale corrections computed for each of the three gases using the B_0 correlation Equations (21B), (22) and (25A). Each table contains columns of figures giving the results of computations by others. The columns marked "Leiden" and "Reichsanstalt" represent computations by W. H. Keesom and K. Onnes (1924) and by W. H. Keesom and W. Tuyn (1938) for the Leiden ensemble of data; the figures under "Reichsanstalt" are taken from Fritz Henning's 1928 article in *Travaux et Mémoires du Bureau International des Poids et Mésure.*[6] In the case of nitrogen there are some comparison figures privately furnished by Professor J. A. Beattie and Doctors B. E. Blaisdell and Joseph Kaye taken from their experimentally ascertained corrections. A few comments on the tables follow.

Table 1. Hydrogen Scale Corrections.

$$t - t_0 = [t2.683\times10^{-4} - T(B_0{}^t - 6.848)8.9865\times10^{-5}]p^{\text{atm}}$$

t	$B_0\frac{\text{cc.}}{\text{g.}}$	$t(2.683\times10^{-4})$	$T(B_0{}^t-6.848)$ 8.9865×10^{-5}	Keyes Δt_{1M}	Henning $\Delta t_{1M}1928$	Keesom and Onnes $\Delta t_{1M}1924$	Keesom and Tuyn $\Delta t_{1M}1938$
200	7.983	0.05366	−0.04826	0.0071	0.022		
100	7.648						
0	6.848						
-50	6.040	−.01341	+0.01620	0.0037	0.007	0.0045	0.002
-100	4.596	−.02683	+0.03504	0.0108	0.016	0.0150	0.009
-150	1.636	−.04024	+0.05769	0.0230	0.028	0.0305	0.022
-200	−6.357	−.05366	+0.08681	0.0436	0.047*	0.0570	0.046
-250	−57.799	−.06707	+0.13453	0.0888		0.1090	0.100

*Interpolated

Table 2. Helium Scale Corrections.

$$t - t_0 \qquad [4.464\times10^{-5}t + T(B_0{}^t - 2.9306)1.7854\times10^{-4}]p_0{}^{\text{atm}}$$

t	$B_0\frac{\text{cc.}}{\text{g.}}$	$4.464\times10^{-5}t$	$T(B_0{}^t-2.9306)$ 1.7854×10^{-4}	Keyes Δt_{1M}	Henning Δt_{1M}	Keesom and Onnes $\Delta t_{1M}1924$	Keesom and Tuyn $\Delta t_{1M}1938$
200	2.794	−.008928	+0.011	0.00348	0.002		
100	2.8636						
0	2.9306						
-50	2.9542	+.00232	−0.00094	0.0017	0.004	0.001	0.002
-100	2.9538	.004464	−0.00072	0.0049	0.011	0.003	0.006
-150	2.8850	.006696	+0.00101	0.0101	0.018	0.008	0.013
-200	2.5606	.008928	+0.00483	0.0181	0.0285*	0.020	0.024
-250	0.0135	.011160	0.01205	0.0305	0.0425*	0.037	0.041
-260	−3.0480	.011606	0.01405	0.0338	0.049†	0.041	0.045
-265	−7.3746	.011829	0.01501	0.0353			
-270	−24.7295	.01205	0.01560	0.0364			0.046

*Interpolated †Extrapolated

In practice, hydrogen in gas thermometry has been replaced by helium, and this gas is now exclusively used in establishing temperatures below the ice point. The scale corrections for hydrogen are therefore somewhat devoid of practical interest. It is none the less interesting to note that substantially satisfactory agreement exists for the correction numbers offered by different computers. A general remark is, however, in order regarding a fundamental difference in method.

Table 3. Nitrogen Scale Corrections.

$$t - t_0 = [2.7426 \times 10^{-3}t - T(B_0{}^t + 0.3567)1.2498 \times 10^{-3}]p_0{}^{\mathrm{atm}}$$

t	$B_0 \frac{\mathrm{cc.}}{\mathrm{g.}}$	$2.7426 \times 10^{-3}t$	$T(B_0{}^t+0.3567)$ 1.2498×10^{-3}	Keyes $\Delta t_{1\mathrm{M}}$	Henning $\Delta t_{1\mathrm{M}}$	Beattie and Blaisdell $\Delta t_{1\mathrm{M}}$	Roebuck and Osterberg $\Delta t_{1\mathrm{M}}$ Eq. (25B)
1000	1.0858	2.7426	−2.2950	0.5895			
600	0.9766	1.6456	−1.4550	0.2508			
500	0.9202	1.3713	−1.2338	0.1809		0.2353 ± .02	
400	0.8400	1.0970	−1.0078	0.1174	0.151	0.1602	0.1196
300	0.7219	0.8228	−0.7726	0.0660	0.073	0.0943	0.0667
200	0.5386	0.5485	−0.5294	0.0250	0.029	0.0387 ± .004	0.0254
100	0.2314						
0	−0.3567						
− 50	−0.8958	−0.1371	+0.1503	0.0174	0.020		0.0174
−100	−1.8407	−0.2743	0.3211	0.0616	0.045		0.0617
−130	−2.8551	−0.3565	0.4469	0.1189	0.094		
−150	+3.9572	−0.4114	0.5542	0.1879			

The formula for the corrections may be written in the following form:

$$t - tg = \left[t \times \frac{T_0 + 100}{100}(B_0{}^{100} - B_0{}^0) - T(B_0{}^t - B_0{}^0) \right] \frac{p_0}{DT} \tag{26}$$

In applying the formula two principal procedures may be employed, as follows: First, discarding any attempt at analytical formulation of the B_0 values, a selection of a $B_0{}^{100}$ and a $B_0{}^0$ value may be taken by averaging or selection on a variety of bases. Using every available B_t datum, the resulting ensemble of scale corrections may be correlated graphically or otherwise. Secondly, an objective method of seeking an adequate analytical form to represent the ensemble of B_0 data (and if they exist, $\mu_0 C_{p_0}$ data also) may be undertaken, followed by a statistical formulation of all the data. The computation of scale corrections then follows its logical course.

The first of these methods has been employed by Keesom and Onnes and by Keesom and Tuyn. The second method is of course followed in this paper, employing all the data, and to a certain extent followed by Henning in using the Reichsanstalt data. It would seem to be preferred provided the equations selected for formulating the data are really good smoothing functions. On the basis of standard statistical tests, for which there is scarcely space for presentation, the formulas here proposed appear to be the "best" the consistency of the ensemble of available data will allow. When better data appear, better formulas can be devised.

In the case of helium the importance of exact scale corrections is increasing rapidly because of the expanding volumes of research at low temperatures. It may be noted from Table 2 that to −150 the figures of Keesom and Tuyn and those of the present computation are satisfactory enough for all practical purposes. Below this temperature, however, the difference of about 0.01 °C persists to −270 °C. A difference of this amount is undesirable in view of the fundamental importance of a precise knowledge of thermodynamic temperatures below 20 °K. The values of Henning and of Keesom and Tuyn are in better agreement, but this circumstance is not decisive in guiding a preference for one set of values over another. The values are based on the experimental data provided by each group, and a different choice of $B_0{}^{100}$ and $B_0{}^0$ on the part of either computer could alter the figures considerably. From the formal statistical point of view the figures

The Kelvin Scale from the Gas Scales by Use of Joule-Thomson Data

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1. General Discussion

The possibility of such a reduction turns upon finding reliable equations connecting the Kelvin temperature (°K), the property used for thermometric measurement, and only such other physical quantities as are all measurable with sufficient precision in the laboratory. It would seem that the two equations proposed by Buckingham[1] are not the only possibilities, nor are these possibilities necessarily restricted to gases. These two equations are:

$$\left(\frac{du}{dv}\right)_T = \lambda = T\left(\frac{dp}{dT}\right)_v - p \tag{1}$$

$$C_p\left(\frac{dT}{dp}\right)_h = \mu C_p = T\left(\frac{dv}{dT}\right)_p - v \tag{2}$$

where u is the intrinsic energy of the gas, h is the enthalpy, and the other symbols have their customary meaning. Both equations may be derived from the first and second laws, the limitation to systems having two free variables and the definitions of the quantities involved. In common with all other equations so founded they may be trusted completely.

Equation (1) relates T, the Kelvin temperature, and p, with a restriction of constant v, and hence is to be employed for the constant-volume gas thermometer (β). The scale for this thermometer is defined by the relation

$$p : \theta \ (v \text{ and } m \text{ constant}) \tag{3}$$

where p is the pressure of the gas at the physical condition of temperature represented by the thermometer reading θ. By simple manipulation, Equation (3) yields

$$\beta = \frac{p_2 - p_1}{p_1(\theta_2 - \theta_1)} = \frac{1}{\theta_1} \ (v, m \text{ constant}) \tag{4}$$

where 1 and 2 are two states between which β is the average coefficient of pressure expansion. Hence for a particular value of θ_1, β is a constant independent of θ_2 and p_2.

If now θ_1 be chosen as the ice point, θ_i, and θ_2 as any other temperature, *θ, the numerical value of θ_i is $\frac{1}{\beta}$, which fixes the zero of this scale in terms of* the ice point and the choice of the particular constant volume, but not of the other reference temperature.

Then from Equation (4) one has

$$p = p_i[1 + \beta(\theta - \theta_i)]_v = p_i\beta\theta \ (v, m \text{ constant}) \tag{5}$$

Equation (1) may be written in the form

$$\frac{d}{dT}\left(\frac{p}{T}\right)_v = \frac{\lambda}{T^2} \tag{6}$$

and hence integrating between T and T_i gives

$$-\frac{p_i}{T_i} = \int_{T_i}^{T} \frac{\lambda}{T^2} dT = \int_{T}^{T_i} \lambda d\frac{1}{T} = (I - I_i) \text{ (}v\text{ constant)}$$

where I and I_i are the values of the integral at the limits T and T_i. Substituting the value of p from Equation (5) into Equation (7), and rearranging gives

$$\theta = \frac{T}{\beta}\left[\frac{1}{T_i} + \frac{1}{p_i}(I - I_i)\right], \tag{8}$$

in which θ is different from T because of the specific properties of the gas as expressed by the values of β, p_i, and the integral $(I - I_i)$. It is also necessary that these three values be measured at one and the same constant value of v and of m, and at which in the further use of this thermometer all measurements must be made in order that these particular reduction figures shall apply.

Reference to Equations (1) and (2) shows them to be identical in form; in (2), p replaces v and μC_p replaces λ. Consequently the whole argument from Equation (1) above may be repeated for Equation (2), leading to the equations

$$\frac{v}{T} - \frac{v_i}{T_i} = \int_{T}^{T_i} \mu C_p d\frac{1}{T} = (I - I_i) \tag{9}$$

$$\theta = \frac{T}{\alpha}\left[\frac{1}{T_i} + \frac{1}{v_i}(I - I_i)\right], \tag{10}$$

in which, as with Equation (8), the difference between T and θ depends on the values of α, v_i, and $(I - I_i)$ for the particular gas. It is also necessary that α, v_i, $(I - I_i)$ be measured at one and the same constant value of p and of m, and at which the gas must be used in further temperature measurements in order that these particular reduction figures shall apply.

2. Kelvin Temperature of Ice Point, T_i

Equation (8) or (10) may be used to calculate T_i by setting $\theta = \theta_s$, $T = T_s$ and defining $\theta_s - \theta_i \equiv 100 \equiv T_s - T_i$—so choosing the size of the degrees—if one knows experimentally the corresponding values of β, p_i, and $(I - I_i)$ or α, v_i, $(I - I_i)$ respectively. The resulting equations are quadratics in T_i and are readily solved by successive approximation, since the closely approximate value of T_i is already known. The available data have been used to calculate T_i by the use of these equations and the results are given in Table 1.

Through a numerical error in 1912, the incorrect factor 1.457 has been used ever since in all our Joule-Thomson work for converting piston gauge readings into atmospheres. The factor should have been 1.410, so that in all previous published work the numbers representing the pressures require multiplying by 0.9677 to express the pressures correctly in international atmospheres. This correction has been made throughout this article.

The correction of this 3 per cent error in the pressure scale affects the different T_i's very differently, being dependent on both sign and size of the difference $(T_i - \theta_i)$. For He this is negative and small, for N_2 and air it is positive and much larger. The correction has had the effect of bringing the T_i's from these separate groups toward one another.

It is here pertinent to ask the size of the error in T_i produced by a definite

Table 1. Kelvin Temperature of Ice Point.

Gas		Experimenters	Date	No. of Readings	T_i	Averages	T_i for One Gas
Air	β	Chappuis[2]	1907	3	273.167	273.167	
Air	α	Chappuis[2]	1907	3	273.209		
		Eumorfopoulos[3]	1908	4	273.122	273.159	273.161
He	β	Holborn, Henning[4]	1911	1	273.075		
		Henning[5]	1921	5	273.204		
		Henning, Heuse[6]	1921	5	273.215		
		Heuse[7]	1926	1	273.199		
		Keesom, v.d. Horst[8]	1927	2	273.118		
		Heuse, Otto[9]	1929	4	273.155		
		Keesom, van Santen[10]	1933	1	273.132		
		Keesom, v.d. Horst, Taconis[11]	1933	3	273.147		
		Kinoshita, Oishi[12]	1937	1	273.169	273.172	
He	α	Henning, Heuse[6]	1921	5	273.159		
		Heuse[7]	1926	1	273.130		
		Heuse, Otto[9]	1929	4	273.167		
		Kinoshita, Oishi[12]	1937	1	273.165	273.160	273.168
N_2	β	Chappuis[13]	1888	1	273.160		
		Chappuis, Harker[14]	1902	4	273.134		
		Chappuis[2]	1907	1	273.188		
		Day, Clement[15]	1908	4	273.226		
		Holborn, Henning[4]	1911	3	273.153		
		Day, Sosman[16]	1912	1	273.111		
		Chappuis[17]	1917	3	273.086		
		Henning[5]	1921	1	273.240		
		Henning, Heuse[6]	1921	3	273.230		
		Keyes, Townshend, Young[18]	1922	1	273.187		
		Heuse, Otto[9]	1929	4	273.177		
		Kinoshita, Oishi[12]	1937	1	273.180		
		Beattie, Blaisdell, Kaye[19]		10	273.196	273.178	
N_2	α	Chappuis[2]	1907	2	273.146		
		Eumorfopoulos[20]	1914	5	273.185		
		Henning, Heuse[6]	1921	3	273.152		
		Heuse, Otto[9]	1929	4	273.138		
		Kinoshita, Oishi[12]	1937	1	273.188	273.163	273.174
		Mean value			273.170		

Ave. divergence of all readings 0.030. Probable error 0.024.

Max. divergence of individual readings $\left\{\begin{array}{l}-0.114\\+0.106\end{array}\right.$ Best value 273.17 ± 0.02.

error in λ or in μC_p. Table 2 presents a group of computations showing such errors. They are almost directly proportional to the pressure at the ice point (p_i) and are much larger for N_2 or air than for He. They are about the same for the α air or N_2 thermometers as for the β. For He they are materially less for the β thermometer. Since $(T_i - \theta_i) = D$ or $= E$ is below 0.4 per cent of T_i,

Table 2.

Gas	Scale	p_i(mm)	$\Delta\mu C_p$ or $\Delta\lambda$ (%)	ΔT_i °K	ΔT_i (%)
Air or N_2	β	1000	2	0.021	0.0076
		500	2	0.011	0.0038
	α	1000	2	0.018	0.0068
		500	2	0.0088	0.0032
He	β	1000	2	0.0005	0.00018
		500	2	0.00026	0.00009
	α	1000	2	0.0042	0.00154
		500	2	0.0021	0.00077

the precision required in the measurement of α and β is at least two hundred and fifty times greater than for μ and λ.

The data in Table 1 are listed chronologically under each gas and type of thermometer. The total 96 readings are averaged, giving equal weight to each reading to give 273.170. The averages for the individual gases, the averages for α and β thermometers, the averages for the individual gases and thermometers (except 273.159) in the column headed "Averages," respectively, differ from 273.170 by less than ±.01°.

This group of readings has been divided into chronological groups in Table 3.

Table 3.

Period	Readings	Ave. T_i	M	–Max. diverg.–	
				+	
Before 1920	35	273.159	0.036	0.118	0.102
1920–1930	43	273.176	0.028	0.083	0.092
1930–date	18	273.180	0.019	0.032	0.048
1920–date	61	273.177	0.026	0.082	0.093
1888–date	96	273.170	0.030	0.106	0.114

Readings: the number of what the individual authors call readings.
M: average divergence of all readings from their group average.
Max. diverg.: maximum divergence of all readings from their group average.

It will be observed in the first three lines of Table 3 that the average and maximum divergences decrease toward the present date. T_i increases similarly. T_i of line 4 compared with T_i of line 1 shows that excluding the readings from before 1920 raises the resulting T_i by 0.007°, whereas excluding those from before 1930 raises it by 0.010°. This certainly suggests that in the future we may have to face still higher results. Since here the whole difference lies within 0.01°, it would seem that the 0.001 figure begins to have significance. It might be noted that in the maximum divergence ± figures, all but one come from the N_2 figures—confirming a previous inference that N_2 offers more difficulty than He in these measurements.

The high value in the "1930-date" line is due entirely to the data from Dr. Beattie's group.[19] The rest of the readings average 273.158. The Beattie data as reduced by our λ data show a definite trend with pressure. This trend may be effectively abolished by a 4-per cent shift in the λ data. But since a second computer checks the first one's λ data to within 1 per cent, a 4-per cent error seems unlikely. We consequently hesitate to choose a most probable value above 273.17 ± 0.02.

The variation of T_i observed here, from both types of thermometers, various values of p_i and v_i, and various gases, are well within the predictable limits of experimental errors. That is, all these measurements provide a single value for T_i—expected of course from the theory, but very comforting to find experimentally.

The probable value of $T_i = 273.17 \pm 0.02$ here differs from 273.16 found previously,[21] first, on account of the correction of the 3-per cent error, and secondly, on account of an increase in the data on α and β.

The values of α and β for $p \doteq 0$ may be determined from Equations (8) and (10). Thus Equation (10) may be written

$$\theta = \frac{T}{\alpha}\left[\frac{1}{T_i} + \frac{1}{v_i}\int_{T}^{T_i} \mu C_p d\frac{1}{T}\right]$$

in which one may replace μC_p by some suitable average value, so that

$$\theta = \frac{T}{\alpha}\left[\frac{1}{T_i} + \frac{(\mu C_p)^1}{v_i}\int_T^{T_i} d\frac{1}{T}\right]$$

Choosing the steam point θ_s and T_s for θ and T, this becomes

$$\theta_i + 100 = \frac{1}{\alpha} + 100 = \frac{1}{\alpha}\left[T_i + 100\right]\left[\frac{1}{T_i} + \frac{(\mu C_p)^1}{v_i}\int_{T_i+100}^{T_i} d\frac{1}{T}\right]$$

From all the experimental data, except around the critical state, μC_p varies slowly and regularly. There is no reason, experimental or theoretical, for expecting μ to grow materially as the pressure is reduced. That μC_p remains finite as $p \doteq 0$ is definitely indicated. That is, for

$$p_i \doteq 0, \frac{(\mu C_p)^1}{v_i} \doteq 0,$$

since v_i increases indefinitely. Inserting this in the above equation one obtains

$$\left[T_i \doteq \frac{1}{\alpha} = \theta_i\right]_{p \doteq 0}$$

and hence the zeros for the two scales—the Kelvin scale and the gas scale at very low pressure—fall at the same physical temperature.

Similarly, one finds from Equation (8)

$$\frac{1}{\beta} + 100 = \frac{1}{\beta}(T_i + 100)\left[\frac{1}{T_i} + \frac{(\lambda)^1}{p_i}\int_{T_i+100}^{T_i} d\frac{1}{T}\right]$$

In all our available data $\left(\frac{\lambda}{p^2}\right)_T$ is constant (He) or nearly so (N_2, air). This constancy also follows readily from van der Waals' equation. Certainly $\left(\frac{\lambda}{p^2}\right)_T$ is finite for $p \doteq 0$. So that $\left(\frac{\lambda}{p_i^2}\right)_T p_i = 0$, for $p_i \doteq 0$.

And as before

$$\left[T_i \doteq \frac{1}{\beta} = \theta_i \doteq \frac{1}{\alpha}\right]_{p \doteq 0}$$

To make use of these relations one must measure α and β at lower and lower pressures. The difficulty of these measurements increases rapidly with decreasing pressures, so that the extrapolation to zero pressure has the greatest uncertainty where the need for precision is greatest.

As a corollary to the above deduction it is evident that generally $\theta = 0$ does not occur at the same physical temperature at which $T = 0$. The temperature at which $\theta = 0$ for He is below that at which $T = 0$, but for N_2 and air it is above.

3. Effect of Laboratory Use of Hydrogen Scale

Equations (8) and (10) contain several experimentally determined quantities whose measurements are normally made using the hydrogen scale. The arguments leading up to both Equations (8) and (10) employ the Kelvin scale. It is necessary to inquire as to the magnitude of the errors introduced by this shift of scales. α and β are the average coefficients between the F.P. and B.P., which are 100° apart on both scales; v_i and p_i are measured at the F.P. which is common to both scales. In the integral in Equation (10), μC_p has the dimensions of volume, the element of temperature appearing in each quantity canceling out in the product. In the integral in Equation (8) λ has the dimensions of pressure, so that in these quantities no difficulties arise. The integration giving $(I - I_i)$ is carried out between limits set in °K whereas the experimental data for λ and for μC_p are related to the hydrogen scale. No precise data are at present available as to the divergence between the Kelvin and the hydrogen scales. It is probable that for most of our range the divergence will have the same sign as for helium and will be somewhat smaller. It will go through zero and reverse sign for probably the lower hundred degrees of our range. For the helium constant-pressure scale, (α) this divergence is $-0.15°$ over our range. If we assume the H_2 scale to be off the Kelvin scale by 1°, calculation shows the resulting error in θ for the N_2 scale to be less than 0.01° at temperatures above -75 °C; but below this the error increases rapidly because of the increasing size of D and of the increasing proportion which 1° is of the temperature. For the helium constant-volume scale, (β), this divergence from the Kelvin scale is about $-0.02°$, so that its effect upon the value of E for nitrogen would be completely negligible.

4. Experimental Data Required

Since the second group of computations, namely $\theta = f(T\,°\mathrm{K})$, could not await the completion of the T_i work, and since the 3-per cent error would undoubtedly raise T_i, the value $T_i = 273.165$ was chosen and used in all the computations of θ.

With T_i so fixed, Equations (8) and (10) can now be used for calculating θ for a series of values of T °K. v_i, the specific volume, is obtained wherever available in the literature. $(I - I_i)$ is the only quantity whose variation with temperature is needed.

$$-I_i = \int_T^{T_i} \lambda d\frac{1}{T} \quad \text{or} \quad \int_T^{T_i} \mu C_p d\frac{1}{T}.$$

These require a knowledge of λ and μC_p as functions of the temperature. Both vary also with the pressure, μC_p rather slowly, but λ very rapidly. To adjust the tabulated values to the working pressure, use was made of the proportionality of λ and p^2, which is sufficiently precise for the adjustment up to a pressure of about 2 atm.

5. Determination of λ

λ is most directly measured by a modification of Joule's free expansion experiment. Joule sought to determine the change of temperature of a gas when it is allowed to change its volume without any interchange of energy with its environment. The modification required is to hold the temperature constant during this change of volume by the addition of just sufficient energy, and then to measure the change in pressure and in volume. From such data the differential coefficient λ may be obtained by appropriate mathematical treatment. Joule's greatest difficulty—the enormous heat capacity of the apparatus—may be cut down by using a pair of concentric spheres[22] as containers, and allowing the gas to escape from the inner one to fill both. The most serious remaining difficulty—the change of temperature with change of stress in the vessel walls—can be minimized by the use of Invar for the walls. A study of the behavior of Invar will allow making corrections for the small residual effect. Study of this experiment has been under way in this laboratory for some years. Dr. H. Dean Baker has a detailed report,[23] to be published shortly, on his analysis and very promising design and construction.

Scattered, fragmentary attempts for such data have been appearing since before Joule's work, but no one has obtained direct data usable for the present problem. Nor have any of the many modifications[24] of this experiment succeeded in obtaining usable data. The only attempt offering a measure of success has been the calculation[25] of λ from the combination of μ, C_p, and pv data.

We attempted this first with air,[25] using only reliable thermodynamic equations; pv data were taken from the literature and used to calculate the derivatives

$$\left(\frac{d(pv)}{dT}\right)_p \quad \text{and} \quad \left(\frac{d(pv)}{dp}\right)_T.$$

These were plotted as functions of p and T and smoothed by cross plotting, using our best judgment to avoid destroying real trends in the data.

Data for C_p at $p = 1$ atm. was spread over the pressure range by use of our isenthalpic curves.

These groups of data were then combined with our μ data to give a group of coefficient—α, the coefficient of volume expansion; $\eta \equiv \left(\frac{dT}{dp}\right)_u$, the free expansion coefficient; γ, the elastic modulus; and $\lambda \equiv \left(\frac{du}{dv}\right)_T$, the rate of change of energy with volume at constant temperature. These coefficients, as functions of temperature and pressure, have an interest on their own account. Attempts to shorten the calculations by combining the equations were not very successful. Hence each of the individual coefficients was calculated. Some of these calculations have lately been repeated with the help of mechanical calculators,* and the improved data have been used in the calculations on the constant-volume nitrogen and air thermometers given below.

With helium,[26] the simplicity of the μ data—its independence of pressure and near independence of temperature—permitted simplifying these calculations and reducing the probable error.

6. Determination of μC_p

The situation with regard to μC_p data is distinctly better than for λ. Data for C_p for the common gases have been accumulating and improving for many years. They have been excellently summarized in Partington and Shilling's book. While more and better data are very desirable, particularly as a function of temperature, there are sufficient for a serious attack on our present problem.

Following Joule and Thomson's original attempts to measure μ, many individual workers have attempted to take such data. This preliminary published work is excellently summarized in Hoxton's paper,[27] in which he gives also the results of his own measurements on air. This preliminary work served mainly to show the complexity of the experimental problem.

About the same time as Hoxton's work a series of workers—Vogel, Noell, and Hausen[28]—at Munich with Professor Knoblauch, carried out a series of throttling experiments on air. Their major interest was the bearing such data have on air-liquefying processes. They covered the field from liquid temperatures to 200 °C and up to 200 atm. The part below room temperature has been used by H. Hausen to construct low-temperature engineering charts[29] of the properties of air. These data are immediately useful for carrying out the reduction of the constant-pressure air thermometer (α) readings to the Kelvin scale. Their data are in reasonable agreement with the Wisconsin data.*

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* Correcting also the 3-per cent scale error in pressure. See above.

Work in this field was begun at Wisconsin in 1905 by E. S. Burnett, who obtained data on air and on carbon dioxide.[30] The work was picked up again by the senior author in 1912, who has carried it nearly continuously to the present with, in later years, a series of partners, J. H. Webb, H. Osterberg, T. A. Murrell, and E. E. Miller.

It became evident almost at the start that there was nothing to be gained by accumulating data without comprehensive proof that the data taken were accurately the data desired. To obtain this assurance, it was necessary to study every phase of the experimental case in detail,[31] and many years were so spent before data judged fit for publication were taken. The primary problem was the calorimetric conditions about the plug, and a big step toward the solution was found in the radial flow type of porous plug.[32] Our form is a cylindrical tube with hemispherical end, made of unglazed porcelain fired to such a temperature that the permeability is that desired, and of a wall thickness sufficient for the necessary strength to carry the higher pressure on the outer surface. Other forms of porous plug can probably be made to give satisfactory data by a sufficiently extended study. But we now know the conditions under which to use the radial flow form. For data to be satisfactory, they must be independent of the rate of flow of gas through the plug. For such proof it is generally necessary to take duplicate data with more than one plug.

In order that either a temperature or a pressure may be measured precisely, it is necessary that it remain constant for a sufficient interval to about the precision desired. Consequently thermostats and barostats have been under experimental study for these years, and have been steadily improved. Every improvement has been apparent immediately in steadier and more consistent data. The performance of a thermostat is very dependent upon such items as the bath stirring, the magnitude and location of the heat exchanges, and their irregularity. Similarly, the barostat performance is very dependent upon the steady performance of the compressor, temperature drifts on regulating valves, line pressure drops, clogging of plug, etc. All of which add up to a very complex interrelated system requiring considerable experience for its effective management.

The desired data should give μ as a function of p and T, with the least amount of experimental work. Two general plans have been followed.

(a) Read experimentally the ratio of ΔT to Δp at a sufficient number of points

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* The senior author's attention has been recently called to the reprinting by E. Justi in "Spezifische Wärme, Enthalpie, Entropie, etc." of Table 14 from his second article on the Joule-Thomson effect in air.[33] As indicated in that article, the source of these data was a large chart from H. Hausen. Unfortunately in reading off the values from the chart serious errors were made in the 100 atm. group. The data for μ at 100 atm. should have been as follows:

	−150 °C	−140	−120	−100	−75	−50	−25	0	+25 °C
Roebuck	+.019	.044	.165	.285	.287	.247	.215	.178	.152
Hausen	−.006	.016	.164	.283	.308	.268	.227	.186	.158

The agreement is markedly improved.

on the (p, T) area, arranging them preferably on p constant and/or T constant lines, so that the $\mu = \frac{\Delta T}{\Delta p}$ surface may be readily fixed. Make the interval Δp small enough so that $\frac{\Delta T}{\Delta p} = \frac{dT}{dp}$ sufficiently closely. Except near the critical state μ changes slowly over the field. The major difficulty is that the experimental irregularity in T and p is too large a part of the Δp and ΔT being measured. This will require, therefore, the finest possible control of T and p. Most workers have found it very difficult to get rid of slow drifts of T_2. Also slow drifts of p are always accompanied by corresponding drifts of T, with a time lag in the latter dependent on the heat capacity between the thermometers. Our experience has been that the most uncertain point on our constant enthalpy curves is the one where Δp is smallest. This method was followed by Joule and Thomson, by Hoxton, by the Munich group, and by most of those who have worked in this field.

(b) Maintain the bath temperature and the initial high pressure constant during a series of readings.[33] Set the pressure p_2 following the plug, successively, at values from near the initial pressure, p_1, to as low as can be managed. Read the temperature, T_2, associated with each p_2. Such a series of readings corresponds to pressure and associated temperature readings made at a series of points through the wall of the plug. They may be immediately plotted as drops from the initial conditions, and the whole resulting curve is characterized by the constant initial enthalpy. The curve may be differentiated by any of the standard methods. The Wisconsin method has been to take ratios of successive and corresponding differences of temperature and of pressure. Thus, except for the differences next the highest pressure, both readings of each difference are made by the same thermometer and piston gauge respectively. Though this does not entirely eliminate the effect of differences of zero, of calibration, and of environment of the pairs of instruments, it nearly does so. As Δp is increased, ΔT increases somewhat proportionately, and so also does the mass flow through the plug. Thus any undesirable heat exchanges which increase as ΔT increases are spread over a correspondingly larger mass flow, and the resulting proportionate error remains nearly unchanged.

The important thermometric gases we have measured are helium, nitrogen, and air.

7. Helium Scales

Helium has the lowest critical temperature of any gas and has a correspondingly simple shape for its (μ, p, T) surface in the region of temperature and pressure attainable in a laboratory. Its isenthalpic curves[34] are accurately straight lines, except approaching liquid air temperature. Its μ is uniformly negative, that is, it shows a rise of temperature on expansion; and this negative μ varies only a little over the range of temperature (500°) covered by our measurements. Since the isenthalpic curves are straight lines, μ is a constant independent of pressure. Several conditions, (a) this lack of dependence of μ on pressure, (b) the fact that the temperature *rises* on isenthalpic expansion, (c) the complete absence of latent heat phenomenon, and (d) the considerable experience in such work already gained, make the μ for helium as accurate as any we have yet measured.

These values of μ, together with C_p and pv data from the literature, have been used to compute λ for helium.[26] These λ values are used to compute $(I - I_t)$ in Equation (7). These results are used in Equation (8) to compute from the constant-volume helium thermometer data, (β), the helium values of T_t given in

Table 1. The value of T_i chosen as most probable (273.165) is next used with the $(I - I_i)$ values, again in Equation (8), to calculate θ for the set of chosen values of T °K in Table 4. Equation (8) with numerical constants fitting this table is also given. The values of θ are uniformly larger than T, and $(T - \theta) = E$ are very small. E is so small that errors up to ±50 per cent in $(I - I_i)$ are required to affect the calculated T_i by 0.01°. They are themselves about as small, in the range of this table, as the unavoidable experimental errors in the use of the helium thermometer.

Table 4. Helium Thermometer.

Constant-volume scale (β); $p_i = 1$ atm.; $T = \theta + E$
$\theta = T[1.000069 + 273(I - I_i)]$

t °C	$-\lambda \times 10^4$	T °K	$(I-I_i)\times 10^7$	θ °A	$-E$	$(-E-.019)$
200	1.6857	473.165	−1.4688	473.179	.014	−.005
100	1.1031	373.165	−0.6790	373.184	.019	.000
50	.6914	323.165	−0.3070	323.185	.020	+.001
0	.3926	273.165	0.0	273.184	.019	.000
−50	.2253	223.165	+0.2534	223.182	.017	−.002

An exactly similar series of steps is carried out with μC_p, Equations (9), (10) and the data for the constant-pressure helium thermometer (α). The resulting data are given in Tables 1 and 5. As in the previous case, θ is larger than T, but $(T - \theta) = D \approx -0.15°$ is now considerably larger. The differences $(T' - \theta') = D' = (-D - 0.155)$, where θ and T are arbitrarily made equal at the steam point, given under $(-D - 0.155)$, are however about the same as in the first thermometer and are also quite negligible when compared to the thermometer experimental errors. Both $(-E - 0.013)$ and $(-D - 0.155)$ are much smaller as well as opposite in sign to the corresponding quantities for nitrogen and air.

Table 5. Helium Thermometer.

Constant-pressure scale (α). $T = \theta + D$
$v_i = 5607$ cc/g; $p_i = 1$ atm.; $\theta = T[1.000571 - 0.04875(I - I_i)]$

t °C	C_p	$-\mu \times 10^2$	T °K	$(I-I_i)\times 10^8$	θ °A	$-D$	$(-D-.155)$
300	1.271	5.97	573.165	6.29	573.316	.151	−.004
250	1.266	6.29	523.165	5.75	523.317	.152	−.003
200	1.264	6.41	473.165	5.08	473.318	.153	−.002
150	1.261	6.45	423.165	4.99	423.319	.154	−.001
100	1.257	6.38	373.165	3.19	373.320	.155	.000
75	1.255	6.35	348.165	2.56	348.320	.155	.000
50	1.254	6.31	323.165	1.83	323.321	.156	+.001
25	1.252	6.24	298.165	0.98	298.321	.156	+.001
0	1.250	6.16	273.165	0.0	273.320	.155	.000
− 50	1.246	6.05	223.165	− 2.58	223.321	.156	+.001
−100	1.243	5.84	173.165	− 6.54	173.319	.154	−.001
−140	1.240	5.40	133.165	−11.52	133.316	.151	−.004
−155	1.239	5.03	118.165	−14.07	118.314	.149	−.006
−180	1.237	4.12	93.165	−19.38	93.306	.141	−.014
−190	1.236	3.80	83.165	−21.90	83.301	.136	−.019

8. Nitrogen Scales

Nitrogen[35] has a critical temperature near the lower limit of our attainable temperature range, and μ goes to zero at about the upper limit. Thus μ has its range of positive values approximately coincident with this attainable temperature

Table 6. Nitrogen Thermometer.

Constant-volume scale (β); $T = \theta + E$
$p_i = 1$ atm.; $\theta = T[0.997126 + 272.4(I - I_i)]$

t °C	$\lambda \times 10^3$	T °K	$(I - I_i) \times 10^6$	θ °A	E	$(E - .790)$
300	2.241	573.165	5.1465	572.321	.849	.059
200	2.415	473.165	4.2882	472.358	.812	.022
150	2.567	423.165	3.6659	422.372	.798	.008
100	2.724	373.165	2.8282	372.380	.790	.000
50	2.882	323.165	1.6661	322.383	.787	−.003
0	3.000	273.165	0.0	272.380	.790	.000
−50	3.164	223.165	−2.5279	222.370	.800	.010

range. In this it is somewhat similar to a whole group of gases—O_2, CO, CH_4, A, NO—whose isenthalpic and μ surfaces form figures very like those for nitrogen.

The experimental and analytical situation is both extensive and complicated. To form any adequate judgment as to the suitability and precision of the μ data for our present purpose, one must examine the original papers.[35] Moreover, the usual calculations leading up to the table for λ have just been completed, and are not yet published. In these calculations the correction for the pressure-scale error has been applied, but the error is present in the published article on nitrogen. Consequently reference must be made here to this latter article and the other articles of the series.

For our present purpose we desire values of λ and μ at pressures from 1/4 atm. to 2 atm. over the largest available temperature range. These values of μ decrease with rising temperature from −170° to 300 °C. The variation of μ with p is given in the table [35] of μ, and is small for the needed range.

λ has been calculated for N_2 as described above for He, with the help of C_p and pv data from the literature. The needed variation of λ with p is given over the small range by the relation $\frac{\lambda}{p^2} = \text{const.}$

Table 7. Nitrogen Thermometer.

Constant-pressure scale (α). $T = \theta + D$
$v_i = 800.0$ cc/g; $p_i = 1$ atm.; $\theta = T[0.997489 + 0.3406(I - I_i)]$

t °C	C_p	$+\mu$	T °K	$(I - I_i) \times 10^3$	θ °A	D	$(D - .686)$
300	.2501	.0139	573.165	2.634	572.240	.925	.239
250	.2495	.0331	523.165	2.593	522.314	.851	.165
200	.2490	.0558	473.165	2.501	472.380	.785	.099
150	.2484	.0868	423.165	2.318	422.437	.728	.042
125	.2480	.1069	398.165	2.171	397.460	.705	.019
100	.2476	.1291	373.165	1.968	372.478	.687	.001
75	.2472	.1555	348.165	1.688	347.491	.674	−.012
50	.2469	.1854	323.165	1.302	322.497	.668	−.018
25	.2467	.2216	298.165	0.762	297.494	.671	−.015
0	.2466	.2655	273.165	0.0	272.479	.686	.000
− 25	.2466	.3223	248.165	− 1.106	247.449	.716	.030
− 50	.2466	.3967	223.165	− 2.762	222.395	.770	.084
− 75	.2469	.5031	198.165	− 5.352	197.308	.857	.171
− 87.5	.2471	.5707	185.665	− 7.216	184.743	.922	.236
−100	.2473	.6487	173.165	− 9.638	172.161	1.004	.318
−112.5	.2474	.7427	160.665	−12.83	159.559	1.106	.420
−125	.2475	.8553	148.165	−17.12	146.929	1.236	.550
−137.5	.2476	.9968	135.665	−23.02	134.261	1.404	.718
−150	.2477	1.265	123.165	−31.68	121.527	1.638	.952
−160	.2478	1.632	113.165	−42.32	111.250	1.915	1.229
−170	.2479	2.004	103.165	−58.28	100.858	2.307	1.621
−180	.2480	2.391	93.165	−81.71	90.338	2.826	2.140

These data for μC_p and λ have been used to calculate T_i as listed in Table 1 and $\theta = f(T)$ as in Tables 6 and 7, exactly as above for He. For the constant volume scale (β) in Table 6, $E = (T - \theta) \approx + 0.8°$ over the range covered. E is thus from 50 to 100 times larger than for He, and is also opposite in sign. This means that about a 1-per cent error in $(I - I_i)$ is needed to produce 0.01° error, both in T_i and in T elsewhere along the scale. The column $(E - .790)$ shows how $(T' - \theta')$ varies along the scale, when $(T_s - \theta_s)$ is made arbitrarily zero. These values of $(E - .790)$ are at least 5 times larger than the corresponding quantities for He. One might surmise that $(E - .790)$ will rise to at least one degree at the gold point.

The base or reference temperature of the high-temperature, or radiation, scale is the melting temperature of gold—the Gold Point. This temperature was measured by Day and Sosman using a constant-volume nitrogen thermometer. Since the radiation scale is closely related to the Kelvin scale, it is very desirable to shift this Gold Point reading to the Kelvin scale. It is surmised that the difference of the two scales is within the experimental errors in the nitrogen thermometer readings. This surmise can be made much more definite by: (a) using Joule-Thomson data on H_2 to calculate the D for N_2 at the Gold Point through the theorem of corresponding states. We plan to measure the Joule-Thomson effect in H_2 as our next gas; (b) repeating the gas thermometer measurements of the Gold Point, using helium as the thermometer gas. It is to be expected that for helium even up to the Gold Point, the increase of $(- D - .155)$ or of $(- E - .013)$ will hardly keep pace with the increase in the errors of the measurement with the helium gas thermometers. That is, such readings of the Gold Point with either helium thermometer will probably give the Kelvin temperature within the errors of the measurements. Because E is so much smaller than D, the constant-volume helium thermometer, (β), is somewhat preferable for such measurement.

The constant-pressure nitrogen scale (α) data for T_i are given in Table 1, and for $\theta = f(T)$ in Table 7. These are calculated using μC_p to calculate $(I - I_i)$, exactly as for He. The values of $(T - \theta) = D$ are very much larger than the corresponding quantities for He, as well as more variable, and are also opposite in sign.

Table 8. Air Thermometer.

Constant-volume scale (β); $T = \theta + E$
$p_i = 1$ atm.; $\theta = T[0.997185 + 272.4(I - I_i)]$

t °C	$\lambda \times 10^3$	T °K	$(I - I_i) \times 10^6$	θ °A	E	$(E - .769)$
200	2.422	473.165	4.1870	472.373	.792	.023
150	2.487	423.165	3.5745	422.386	.779	.010
100	2.610	373.165	2.7678	372.396	.769	.000
75	2.712	348.165	2.2560	347.399	.766	−.003
50	2.821	323.165	1.6414	322.400	.765	−.004
25	2.897	298.165	0.8974	297.399	.766	−.003
0	2.940	273.165	0.0	272.396	.769	.000
− 25	2.959	248.165	−1.0883	247.393	.772	.003
− 50	2.960	223.165	−2.4244	222.389	.776	.007
− 75	2.947	198.165	−4.0932	197.386	.779	.010
−100	2.921	173.165	−6.2309	172.384	.781	.012

The values of $(D - .479)$ for N_2 are also much larger than $(- D - .155)$ for He: at 300 °C the former is 60 times the latter. Both are growing numerically with rising temperature. If the growth continues linearly to the Gold Point $(D - .479)$ for N_2 will become 1.25°, and it is growing faster than linearly.

9. Air Scales

Since air is four-fifths nitrogen, the Joule-Thomson data for air[31,25] are very similar to those for nitrogen.[35] Hence only the data directly applicable to the case are given here. These are tabulated in Tables, 1, 8, and 9 with the resulting θ, E, and D values. Although very like the nitrogen data, these are yet definitely different. The presence of oxygen and argon, of critical temperatures higher than that of nitrogen, is sufficient reason for this.

Table 9. Air Thermometer.

Constant-pressure scale (α); $T = \theta + D$
$v_i = 773.4$ cc/g; $p_i = 1$ atm.; $\theta = T[0.997344 + 0.3523(I - I_i)]$

t °C	C_p	μ	T °K	$(I-I_i)\times 10^3$	θ °A	D	$(D-.725)$
280	.2458	.0307	553.165	2.697	552.221	.944	.219
250	.2453	.0415	523.165	2.659	522.266	.899	.174
200	.2443	.0456	473.165	2.570	472.336	.829	.104
150	.2434	.0958	423.165	2.391	422.397	.768	.043
100	.2424	.1371	373.165	2.021	372.440	.725	.000
75	.2419	.1633	348.165	1.732	347.453	.712	−.015
50	.2415	.1949	323.165	1.335	322.459	.706	−.019
25	.2410	.2344	298.165	0.778	297.455	.710	−.015
0	.2405	.2751	273.165	0.0	272.440	.725	.000
− 25	.2399	.3264	248.165	− 1.101	247.410	.755	.030
− 50	.2394	.3879	223.165	− 2.700	222.360	.805	.080
− 75	.2390	.4772	198.165	− 5.117	197.281	.884	.159
−100	.2385	.5940	173.165	− 8.969	172.158	1.007	.282
−120	.2381	.7303	153.165	−13.92	152.009	1.156	.431
−140	.2376	.9824	133.165	−22.17	131.772	1.393	.668

As for He and N_2, E varies very slowly, so that $(E - .769)$ is only one-fortieth of a degree at 200 °C. At the higher temperatures, D for air is larger than for N_2, but by −100 °C it has become about equal and is smaller at still lower temperatures.

We wish to thank Dr. J. A. Beattie for his courtesy in sending us the results of their measurements in advance of publication; G. H. Ward and M. M. Vance, who carried out the calculations on N_2; the National Youth Administration which made it possible; and the Wisconsin Alumni Research Foundation for their support of this research project.

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The Thermodynamic Temperature of the Ice Point*

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1. Introduction

During the decade 1890 to 1900, experimentation at very high and very low temperatures and increased accuracy in measurements at ordinary temperatures heightened interest in gas thermometry, the primary means for determining temperature. The precise gas thermometric investigations of Chappuis, who published on this subject from 1887 to 1917, not only gave data from which a fair estimate of the thermodynamic temperature of the ice point could be made, but also furthered interest in this type of work and in the determination of those properties of gases necessary for the correction for gas imperfection.

Two types of gas thermometers—constant-volume and constant-pressure—have been in general use. In each the experimental instrument differs from the idealized one in important respects, and the real thermometric fluid differs from a perfect one.

In the idealized constant-volume, or constant-density, gas thermometer a definite mass of gas is enclosed in a bulb of invariant volume V_0, the density of the gas being constant throughout the bulb. The pressures p_0 and p_{100} of the gas are measured while the bulb is thermostated at 0 and at 100 °C, respectively. The mean thermal coefficient of pressure increase from 0 to 100 °C at constant volume, α_v, of the thermometric fluid is defined by the relation:

$$\alpha_v = \frac{p_{100} - p_0}{100\, p_0} = \frac{p_{100} V_{100} - p_0 V_0}{100\, p_0 V_0}\,; \; (V_{100} = V_0). \tag{1}$$

In the idealized constant-pressure gas thermometer a definite mass of gas is enclosed in a bulb of variable volume, the pressure being constant throughout the system and having the value p_0. The volumes V_0 and V_{100} of the gas are measured while the bulb is thermostated at 0 and at 100 °C, respectively, the pressure being p_0 at 0 °C and being made equal to p_0 at 100 °C by adjustment of V_{100}. In actual practice the pressure at 100 °C is adjusted to p_0 by withdrawal of gas from the bulb into a pipette at, say, 0 °C. The mean thermal coefficient of expansion from 0 to 100 °C at constant pressure, α_p, of the thermometric fluid is defined by the relation:

$$\alpha_p = \frac{V_{100} - V_0}{100\, V_0} = \frac{p_{100} V_{100} - p_0 V_0}{100\, p_0 V_0} = \frac{D_0 - D_{100}}{100\, D_{100}}\,; \; (p_{100} = p_0), \tag{2}$$

where D_0 and D_{100} are the densities of the gas in the bulb at 0 and 100 °C, respectively, and are the quantities computed in measurements with the constant-pressure gas thermometer as carried out in practice.

The general thermodynamic theory of real and perfect gases gives the result that for any real gas:

$$\lim_{p_0 \to 0} \alpha_v = \lim_{p_0 \to 0} \alpha_p = \alpha = \frac{1}{T_0}, \tag{3}$$

where α is the thermometric coefficient, α_v or α_p, of a perfect gas, and T_0 is the thermodynamic temperature of the ice point.

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 434.

2. Correction for the Imperfection of the Experimental Instrument

In both types of gas thermometers the effects of the following deviations of the experimental from the idealized instrument must be taken into account in the computation of the pressures or volumes (densities), used in Equations (1) and (2), from the observed quantities:

(a) The presence of some of the gas at temperatures different from the bulb (the dead-space correction).

(b) The variation of the volume of the system with temperature, pressure, and the position and shape of the mercury meniscus in the short arm of the manometer (the volume-variation correction).

(c) The effect of the gravitational field (the gravitational correction).

The fundamental equation[1] for correction for the above effects is:

$$N = \frac{pV}{A_b + B_b p + C_b p^2} = p' \int_{x_A}^{x_S} \frac{(1+\phi)a\,dx}{A + B(1+\phi)p' + C(1+\phi)^2} \tag{4}$$

where:

N = number of moles of gas in the system;

p = pressure in the equivalent idealized gas thermometer;

V = volume of the equivalent idealized gas thermometer;

p' = pressure at mercury meniscus in short arm of manometer;

x = linear distance measured along axis of gas thermometer system (bulb, capillaries, etc.) from the bottom of the bulb, x_A, to the mercury meniscus, x_S, in the short arm of the manometer;

$a = a(x)$ = cross-section of system at x in the plane perpendicular to x;

A, B, C, = parameters in the equation of state $pV = A + Bp + Cp^2$ of the thermometric gas. They are functions of temperature; and hence, in the right-hand side of Equation (4), they are functions of x;

$\phi = \phi(x)$ = gravitational correction function such that $\pi = p'(1+\phi)$, where π is the pressure at x;

b = subscript to denote the value of a quantity at the temperature of the bulb of the equivalent idealized gas thermometer.

The right-hand expression of Equation (4) gives the number of moles of gas in the experimental gas thermometer and the middle expression, the number of moles in the equivalent idealized instrument. The integral can be evaluated as a sum of terms after the integrand has been expanded and terms introducing an error of less than one part in 10^7 neglected.

For the constant-volume thermometer, p is the corrected pressure to be used in Equation (1) and V is the constant volume of the system at some selected set of standard conditions. Both p_0 and p_{100} are corrected by this formula.

For the constant-pressure thermometer, V is the corrected volume to be used in Equation (2) and p is the standard pressure (p_0). Both V_0 and V_{100} are to be corrected by this formula.

3. Thermodynamic Theory of Real Gases

A basis for the thermodynamic treatment of real gases and mixtures of real gases has been given,[2] the results being derived from two assumptions concerning the isothermal behavior of real gases. For the present purpose a simpler treatment suffices, since only pure gases are involved.

Let us assume:

(a) As the pressure on a real gas approaches zero at constant temperature, the enthalpy, H, and its derivative, $(\partial H/\partial p)_T$, remain finite.

(b) As the pressure on a real gas approaches zero at constant temperature, the pressure-volume product, pV, and its derivative, $(\partial pV/\partial p)_T$, remain finite.

These two isothermal assumptions are substantiated by all of the experimental data existent on real gases. Thus at low pressures:

$$H = a + bp + \ldots\ldots, \tag{5}$$

$$pV = A + Bp + \ldots\ldots, \tag{6}$$

where a, b, A, B are temperature functions and terms of the order of p^2 have been neglected. If the left-hand side of the relation,

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

is evaluated from Equation (5), and the right-hand side from Equation (6), there results:

$$0 + b + \ldots\ldots = \frac{1}{p}\left(A - T\frac{dA}{dT}\right) + \left(B - T\frac{dB}{dT}\right) \tag{8}$$

This relation can hold for all values of p and T only if

$$A - T\frac{dA}{dT} = 0. \tag{9}$$

Integration of (9) yields

$$RT, \tag{10}$$

where T is thermodynamic temperature and R a constant. The equation of state for a real gas thus becomes:

$$pV = RT + Bp + \ldots\ldots \tag{11}$$

In the determination of the second virial coefficient, B, from the isothermal compressibility data on a gas, the first term, A, should not be determined at each temperature from the compressibility data, but should be placed equal to A_0T/T_0, where T_0 is the thermodynamic temperature of some one isotherm, say, 0 °C. Then $pV - A_0T/T_0$ should be used to determine the virial coefficients, B, C, etc. The two methods sometimes give quite different results.

At zero pressure, Equation (11) reduces to

$$pV = RT, \tag{12}$$

the equation of state of a perfect gas. Evaluation of the pV products of Equations (1) and (2) from Equation (12) gives in either case:

$$\frac{RT_{100} - RT_0}{100\,RT_0} \quad \frac{1}{T_0}, \tag{13}$$

where α is the thermometric coefficient at constant volume or at constant pressure for an ideal gas, and T_0 the thermodynamic temperature of the ice point.

4. Correction of Thermometric Coefficients for the Imperfection of the Gas

(a) Joule-Thomson and Compressibility Method. *Constant-pressure gas thermometer.*—Let

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \tag{14}$$

be the ratio of the decrease in temperature, $-dT$, produced in a fluid by a decrease in pressure $-dp$ at constant enthalpy H in the Joule-Thomson or porous plug experiment. Then

$$\mu = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p}, \tag{15}$$

and since $(\partial H/\partial T)_p$ is the heat capacity at constant pressure C_p:

$$\sigma = \mu C_p = -\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_p - V = -\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_p. \tag{16}$$

The third equality results from general thermodynamic theory, and the fourth from mathematics. Thus

$$\left[d\frac{V}{T} = -\sigma\, d\frac{1}{T}\right]_{p=\text{constant}}, \tag{17}$$

and integration from 0 to 100 °C at constant pressure gives:

$$\frac{V_{100}}{T_{100}} \quad \frac{V_0}{T_0} \quad -\int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right), \tag{18}$$

where the integral is to be evaluated along a constant-pressure curve. Substitution of the value of V_{100} obtained from Equation (18) into Equation (2) gives:

$$\frac{1}{T_0} - \frac{T_{100}}{100\, V_0}\int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right), \tag{19}$$

$$\frac{1}{T_0} - \frac{T_{100}\, p_0}{100\, RT_0}\int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right), \tag{20}$$

$$\alpha - \frac{1 + 100\alpha}{100}\,\frac{p_0}{R}\int_{T_0}^{T_{100}} \sigma d\left(\frac{1}{T}\right), \tag{21}$$

by Equation (13). The integral is to be evaluated along the constant-pressure line, p_0, to which α_p refers; and p_0 is to be expressed in the same pressure units and σ in the same volume and mass units as RT. The second term on the right-hand side of Equation (21) is small compared with the first term at pressures used in gas thermometers, so that an approximate value of α can be assumed for the first approximation and then corrected.

From Equations (5) and (16)

$$\sigma_1 = -b + \ldots\ldots \tag{22}$$

so that at low pressures σ is finite, and

$$\lim_{p_0 \to 0} \alpha_1 \quad \alpha = \frac{\;}{T_0} \tag{23}$$

from Equations (20) and (21).

Constant-volume Gas Thermometer.—Let

$$= -\left(\frac{\partial T}{\partial V}\right)_U \tag{24}$$

be the ratio of the decrease in temperature, $-dT$, produced in a fluid by an increase in volume, dV, at constant energy, U, in the Joule or free-expansion experiment.

Then

$$\eta = \frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}, \tag{25}$$

and since $(\partial U/\partial T)_V$ is the heat capacity at constant volume, C_v:

$$\lambda = \eta C_v = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - \qquad - \left[\frac{\partial(p/T)}{\partial(1/T)}\right]_V. \tag{26}$$

The third equality results from general thermodynamic theory, and the fourth from mathematics. Thus

$$\left[d\frac{p}{T} = -\lambda d\frac{1}{T}\right]_{V=\text{constant}}; \tag{27}$$

and integration from 0 to 100 °C at constant volume gives:

$$\frac{p_{100}}{T_{100}} - \frac{p_0}{T_0} = -\int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right), \tag{28}$$

where the integral is to be evaluated at constant volume. Substitution of the value of p_{100} obtained from Equation (28) into Equation (1) gives:

$$\alpha_v = \frac{1}{T_0} - \frac{T_{100}}{100\,p_0}\int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right) \tag{29}$$

$$\frac{1+100\alpha}{100\alpha p_0}\int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right) \tag{30}$$

by Equation (13). The integral is to be evaluated along the constant-volume (or density) line to which α_v refers (the density of the gas at p_0 and T_0); and λ is to be expressed in the same pressure units as p_0.

From the definition of H,

$$H = U + pV, \tag{31}$$

and Equations (26), (5), and (11), there results for a gas at low pressures:

$$\lambda = -\frac{(b-B)}{RT}p^2 + \qquad \cdot\cdot \tag{32}$$

Hence,

$$\lim_{p_0\to 0} \alpha_v = \qquad \frac{}{T_0} \tag{33}$$

from Equations (29), (30), and (32).

As a matter of fact λ is never computed from η and C_v because of the difficulty of measurement of η. Keyes and Sears[3] have made some measurements of η for carbon dioxide, and Roebuck[4] mentions an attempt to determine this quantity. For gas thermometric corrections, λ is always computed from Joule-Thomson and compressibility data, as has been done by Roebuck.[4]

(b) Compressibility or B Value Method.—Substitution from the equation of state (11) into Equations (1) and (2) and use of the relations

$$p_{100} = p_0 \text{ (constant-pressure thermometer)} \tag{34}$$

$$p_{100} = (1+100\alpha)p_0 = \frac{T_{100}}{T_0}p_0 \text{ (constant-volume thermometer)} \tag{35}$$

give, after division and simplification:

$$\alpha_p = \frac{1}{T_0} + \frac{B_{100} - B_0 T_{100}/T_0}{100RT_0} p_0 \tag{36}$$

$$= \alpha + \frac{B_{100} - B_0(1 + 100\alpha)}{100RT_0} p_0 = \alpha + F_p p_0 \tag{37}$$

$$\frac{1}{T_0} + \frac{T_{100}}{100T_0} \frac{B_{100} - 1}{RT_0} p_0 \tag{38}$$

$$= \alpha + \frac{1 + 100\alpha}{100} \frac{B_{100} - B_0}{RT_0} p_0 = \alpha + F_v p_0. \tag{39}$$

It will be noted that these expressions are in agreement with the conditions given in Equation (3). The terms in p_0^2 of Equations (36) to (39) which have been dropped are much smaller than the experimental error in α_v or α_p.

(c) Extrapolation Method.—When α_v or α_p has been measured at several different pressures for a gas we may extrapolate to zero pressure by expressing α_v or α_p as a linear function of the pressure. The use of a quadratic equation is never warranted by the accuracy of any data existing at the present time, and would in fact introduce an error in the extrapolated value of α by magnifying the effects of the experimental error.

Table 1. Values of F_v and F_p Derived by Several Authors.

$$\frac{1 + 100\alpha}{100} \frac{B_{100} - B_0}{RT_0}$$

$$F_p = \frac{1}{100} \frac{B_{100} - B_0(1 + 100\alpha)}{RT_0}$$

Units of F_v and F_p : meters Hg^{-1} °K^{-1}.

Gas	Keyes[1] 10^7F_v	Keyes[1] 10^7F_p	Keesom, Tuyn[2] 10^7F_v	Keesom, Tuyn[2] 10^7F_p	Heuse, Otto[3] 10^7F_v	Heuse, Otto[3] 10^7F_p
He	−2.16	−26.79	−3.61	−26.9	−2.7	−27.4
H_2	+12.76	−20.08	+11.3	−21.4	+11.7	−21.4
N_2	+132.12	+118.19	+131.3	+117.9	+133.67	+120.30
Ne			+12.6	−13.6	+14.9	−11.5

Notes and References:

[1] F. G. Keyes, this book, pp. 45-59.
The B values were computed from Keyes' equations:

$B_{He} = 4.002\ [16.4873T^{-0.25} - 74.09T^{-0.75} - 24.6T^{-1.25}]$ ml. mole^{-1}

$B_{H_2} = 2.0156\ [60.000T^{-0.25} - 397.25T^{-0.75} - 2282.056T^{-1.25}]$ ml. mole^{-1}

$B_{N_2} = 28.016\ [10.08T^{-0.25} - 766.115T^{-1} - 1.7545 \times 10^8 T^{-4}]$ ml. mole^{-1}

and the values: R=62.360 ml. meter Hg mole^{-1} °K^{-1}; $T_0 = 1/\alpha = 273.16$ °K. Keyes'[1] equations were derived from a study of the compressibility and Joule-Thomson data.

[2] W. H. Keesom and W. Tuyn, Kamerlingh-Onnes Lab., Univ. of Leiden, Supplement No. 78, 85 pp. (1936). Keesom and Tuyn derived their B values from a consideration of those determined of 0 and at 100 °C by several authors, the Leiden values being given greatest weight.

[3] W. Heuse and J. Otto, *Ann. der Physik* (5), **2**, 1012-1030 (1929). Heuse and Otto computed their B values from the compressibility data determined at the Physikalisch-Technischen Reichsanstalt. They give for nitrogen F_v = 137.4 and F_p = 123.5. The values given in this table for nitrogen under the heading "Heuse, Otto" were computed from B values determined by the present author from the P. T. R. compressibility data in the temperature range 0 to 400 °C and under 100 atmospheres, pressure. The method of least squares was used to determine B and C in the equation $pV = A + Bp + cp^2$ at each temperature, A being put equal to A_0 (t °C + 273.16)/273.16. The B values were then smoothed analytically. There resulted for N_2: $B_0 = -10.445$, $B_{100} = 6.223$ ml. mole

The Joule-Thomson method of correction for gas imperfection was the preferred method in the early part of the present century because of the lack of good compressibility data; at the present time the B value method of correction is almost universally used. The extrapolation method was used with fair success by

(Text cont'd on p. 82)

Table 2. Kelvin Temperature of the Ice Point Derived from Gas Thermometry Measurements on Helium, Hydrogen, Nitrogen, and Neon During the Period 1900 to 1937.

p_0 = ice point pressure (meters of mercury).
α_g = observed mean coefficient, α_v or α_p, as designated in subheadings.
α_v = mean coefficient of pressure increase from 0 to 100 °C at constant volume.
α_p = mean coefficient of thermal expansion from 0 to 100 °C at constant pressure.
α = ideal gas mean coefficient.
T_0 = Kelvin temperature of ice point.

The values of F_v and F_p used are given in Table 1.

Author	Date	Bulb	p_0	$10^7\alpha_g$	Ideal gas mean coefficient (α °K^{-1}) Kelvin temperature of the ice point (T_0 °K)					
					Source of F values used to correct for gas imperfection					
					Keyes		Keesom, Tuyn		Heuse, Otto	
					$10^7\alpha$	T_0	$10^7\alpha$	T_0	$10^7\alpha$	T_0
					Helium α_v (constant-volume gas thermometer)					
Holborn, Henning	1911	59^{III} glass	0.613	36618	36619.3	273.080	36620.2	273.073	36619.7	273.077
Henning	1921	59^{III} glass	.801	36597	36598.7	.234	36599.9	.225	36599.2	.230
			.777	36603	36604.7	.189	36605.8	.181	36605.1	.186
			.748	36600	36601.6	.212	36602.7	.204	36602.0	.209
			.709	36604	36605.5	.183	36606.6	.175	36605.9	.180
			.660	36597	36598.4	.236	36599.4	.229	36598.8	.233
Henning, Heuse	1921	59^{III} glass	1.1165	36600	36602.4	.206	36604.0	.194	36603.0	.202
			1.1029	36601	36603.4	.199	36605.0	.187	36604.0	.194
			0.7601	36598	36599.6	.227	36600.7	.219	36600.1	.223
			.5205	36599	36600.1	.223	36600.9	.217	36600.4	.221
			.5048	36595	36596.1	.253	36596.8	.248	36596.4	.251
Keesom, v.d.Horst	1927	16^{III} glass	.9866	36611	36613.1	.126	36614.6	.115	36613.7	.122
			.9742	36611	36613.1	.126	36614.5	.116	36613.6	.123
Heuse, Otto	1929	59^{III} glass	.9945	36604	36606.1	.179	36607.6	.167	36606.7	.174
			.7272	36611	36612.6	.130	36613.6	.123	36613.0	.127
			.5331	36602	36603.2	.200	36603.9	.195	36603.4	.199
			.3902	36611	36611.8	.136	36612.4	.132	36612.1	.134
Keesom, v.d.Horst, Taconis	1933	2954^{III} glass	.9670	36607.3	36609.4	.154	36610.8	.143	36609.9	.150
			.7500	36607.9	36609.5	.153	36610.6	.145	36609.9	.150
			.5079	36608.6	36609.7	.152	36610.4	.146	36610.0	.149
Kinoshita, Oishi	1937	1565^{III} glass	1.000	36604	36606.2	.178	36607.6	.167	36606.7	.174
					Helium α_p (constant-pressure gas thermometer)					
Henning, Heuse		59^{III} glass	1.1165	36581	36610.9	273.143	36611.0	273.142	36611.6	273.137
			1.1029	36582	36611.5	.138	36611.7	.137	36612.2	.133
			0.7601	36591	36611.4	.139	36611.4	.139	36611.8	.136
			.5205	36603	36616.9	.098	36617.0	.097	36617.3	.095
			.5048	36589	36602.5	.205	36602.6	.205	36602.8	.203
Heuse, Otto		59^{III} glass	.9945	36579	36605.6	.182	36605.8	.181	36606.2	.178
			.7272	36587	36606.5	.176	36606.6	.175	36606.9	.173
			.5331	36594	36608.3	.162	36608.3	.162	36608.6	.160
			.3902	36597	36607.5	.168	36607.5	.168	36607.7	.167
Kinoshita, Oishi	1937	1565^{III} glass	1.000	36580	36606.8	.173	36606.9	.173	36607.4	.169
					Hydrogen α_v (constant-volume gas thermometer)					
Chappuis	1888	Pt. Ir.	0.9990	36625.3	36612.6	273.130	36614.0	273.120	36613.6	273.123
Onnes, Boudin	1900	16^{III} glass	1.0983	36627	36613.0	.127	36614.6	.115	36614.1	.119
Travers, Jaquerod	1903	Soft glass	0.7065	36624.6	36615.6	.108	36616.6	.100	36616.3	.102
			.6961	36625.2	36616.3	.102	36617.3	.095	36617.1	.096
			.6945	36626.1	36617.2	.096	36618.3	.087	36618.0	.090
			.5203	36626.8	36620.2	.073	36620.9	.068	36620.7	.070
			.3480	36613.3	36608.9	.158	36609.4	.154	36609.2	.155
Chappuis	1907	Verre dur	1.0011	36621.7	36608.9	.158	36610.4	.146	36610.0	.149
		Pt. Ir.	1.0005	36629.6	36616.8	.099	36618.3	.087	36617.9	.090
Holborn, Henning	1911	59^{III} glass	0.6233	36624	36616.0	.105	36617.0	.097	36616.7	.099
Henning	1913	59^{III} glass	.7401	36614	36604.6	.190	36605.6	.182	36605.3	.184
Henning	1921	59^{III} glass	.815	36606	36595.6	.257	36596.8	.248	36596.5	.250
Henning, Heuse	1921	59^{III} glass	1.0953	36623	36609.0	.157	36610.6	.145	36610.2	.148
			0.5082	36612	36605.5	.183	36606.3	.177	36606.1	.179

Table 2.—(*Continued*)

Author	Date	Bulb	p_0	$10^7\alpha_g$	Ideal gas mean coefficient (α °K^{-1}) Kelvin temperature of the ice point (T_0 °K)					
					Source of F values used to correct for gas imperfection					
					Keyes		Keesom, Tuyn		Heuse, Otto	
					$10^7\alpha$	T_0	$10^7\alpha$	T_0	$10^7\alpha$	T_0
Hydrogen α_v (constant-volume gas thermometer)—(*Continued*)										
Heuse, Otto	1929	$59^{\rm III}$ glass	.9945	36621	36608.3	273.162	36609.8	273.151	36609.4	273.154
			.7272	36620	36610.7	.144	36611.8	.136	36611.5	.138
			.5331	36613	36606.2	.178	36607.0	.172	36606.8	.173
			.3902	36617	36612.0	.134	36612.6	.130	36612.4	.132
Kinoshita, Oishi	1937	$1565^{\rm III}$ glass	1.000	36619	36606.2	.178	36607.7	.167	36607.3	.170
Hydrogen α_p (constant-pressure gas thermometer)										
Chappuis	1907	Pt. Ir.	1.0005	36600.4	36620.5	273.072	36621.8	273.061	36621.8	273.061
Henning, Heuse	1921	$59^{\rm III}$ glass	1.0953	36590	36612.0	.134	36613.4	.124	36613.4	.124
			0.5082	36602	36612.2	.133	36612.9	.128	36612.9	.128
Heuse, Otto	1929	$59^{\rm III}$ glass	.9945	36589	36609.0	.157	36610.3	.147	36610.3	.147
			.7272	36593	36607.6	.167	36608.6	.160	36608.6	.160
			.5331	36604	36614.7	.114	36615.4	.109	36615.4	.109
			.3902	36604	36611.8	.136	36612.4	.132	36612.4	.132
Kinoshita, Oishi	1937	$1565^{\rm III}$ glass	1.000	36586	36606.1	.179	36607.4	.169	36607.4	.169
Nitrogen α_v (constant-volume gas thermometer)										
Chappuis[a]	1888	Pt. Ir.	0.9959	36746.6	36615.0	273.112	36615.8	273.106	36613.5	273.123
Chappuis, Harker	1902	Verre dur	.7935	36718.0	36613.2	.126	36613.8	.121	36611.9	.135
			.5329	36684.7	36614.3	.117	36614.7	.114	36613.5	.123
		Porcelain	.5288	36681.1	36611.2	.140	36611.7	.137	36610.4	.146
			.3920	36677.0	36625.2	.036	36625.5	.034	36624.6	.041
Chappuis	1907	Pt. Ir.	1.0019	36744.2	36611.8	.136	36612.7	.129	36610.3	.147
Day, Clement[b]	1908	Pt. Ir.	0.985	36730	36599.9	.225	36600.7	.219	36598.3	.237
			.744	36700	36601.7	.211	36602.3	.207	36600.5	.220
			.550	36680	36607.3	.170	36607.8	.166	36606.5	.176
			.314	36650	36608.5	.161	36608.8	.158	36608.0	.164
Holborn, Henning	1911	$59^{\rm III}$ glass	.6312	36706	36622.6	.055	36623.1	.052	36621.6	.063
			.6213	36699	36616.9	.098	36617.4	.094	36616.0	.105
		Fused silica	.6206	36684	36602.0	.209	36602.5	.205	36601.0	.217
Day, Sosman	1912	Pt. Rh.	.5018	36685	36618.7	.085	36619.1	.082	36617.9	.090
Chappuis	1917	Fused silica	.564	36699	36624.5	.041	36624.9	.038	36623.6	.048
			.562	36695.9	36621.6	.063	36622.1	.059	36620.8	.069
			.553	36694.3	36621.2	.066	36621.7	.062	36620.4	.072
Henning	1921	$59^{\rm III}$ glass	.756	36703	36603.1	.201	36603.7	.196	36601.9	.210
Henning, Heuse	1921	$59^{\rm III}$ glass	1.1053	36752	36606.0	.179	36606.9	.173	36604.3	.192
			0.5114	36675	36607.4	.169	36607.9	.165	36606.6	.175
			.2203	36626	36596.9	.247	36597.1	.246	36596.6	.249
Keyes, Townshend, Young	1922	Fused silica	.6538	36696	36609.6	.152	36610.2	.148	36608.6	.160
Heuse, Otto	1929	$59^{\rm III}$ glass	.9945	36740	36608.6	.160	36609.4	.154	36607.1	.171
			.7272	36709	36612.9	.128	36613.5	.123	36611.8	.136
			.5331	36671	36600.6	.220	36601.0	.217	36599.7	.226
			.3902	36673	36621.4	.064	36621.8	.061	36620.8	.069
Kinoshita, Oishi	1937	$1565^{\rm III}$ glass	1.000	36745	36612.9	.128	36613.7	.122	36611.3	.140
Nitrogen α_p (constant-pressure gas thermometer)										
Chappuis	1907	Pt. Ir.	1.3868	36777.5	36613.6	273.123	36614.0	273.120	36610.7	273.144
			1.0019	36731.5	36613.1	.126	36613.4	.124	36611.0	.142
Eumorfopoulos	1914	Fused silica	0.792	36700.5	36606.9	.173	36607.1	.171	36605.2	.185
			.784	36701.9	36609.2	.155	36609.5	.153	36607.6	.167
			.757	36699.1	36609.6	.152	36609.8	.151	36608.0	.164
			.415	36658.7	36609.7	.152	36609.8	.151	36608.8	.158
			.395	36656.1	36609.4	.154	36609.5	.153	36608.6	.160
Henning, Heuse	1921	$59^{\rm III}$ glass	1.1053	36742	36611.4	.139	36611.7	.137	36609.0	.157
			0.5114	36679	36618.6	.085	36618.7	.085	36617.5	.093
			.2203	36630	36604.0	.194	36604.0	.194	36603.5	.198
Heuse, Otto	1929	$59^{\rm III}$ glass	.9945	36734	36616.5	.101	36616.7	.099	36614.4	.117
			.7272	36699	36613.1	.126	36613.3	.125	36611.5	.138
			.5331	36668	36605.0	.187	36605.1	.186	36603.9	.195
			.3902	36664	36617.9	.090	36618.0	.090	36617.1	.096
Kinoshita, Oishi	1937	$1565^{\rm III}$ glass	1.000	36729	36610.8	.143	36611.1	.141	36608.7	.159

Table 2.—(*Continued*)

ior	Date	Bulb	p_0	$10^7\alpha_0$	Ideal gas mean coefficient (α °K^{-1}) Kelvin temperature of the ice point (T_0 °K) Source of F values used to correct for gas imperfection					
					Keyes		Keesom, Tuyn		Heuse, Otto	
					$10^7\alpha$	T_0	$10^7\alpha$	T_0	$10^7\alpha$	T_0
Neon α_v (constant-volume gas thermometer)										
Heuse	1926	59^{III} glass	1.0070	36613			36600.3	273.222	36598.0	273.239
			0.6870	36605			36596.3	.252	36594.8	.263
Heuse, Otto	1930	59^{III} glass	.9945	36623.4			36610.9	.143	36608.6	.160
Kinoshita, Oishi	1937	1565^{III} glass	1.000	36616			36603.4	.199	36601.1	.216
Neon α_p (constant-pressure gas thermometer)										
Heuse	1926	59^{III} glass	1.0070	36602			36615.7	273.107	36613.6	273.123
			0.6870	36604			36613.3	.125	36611.9	.135
Heuse, Otto	1930	59^{III} glass	.9945	36600.8			36614.3	.117	36612.2	.133
Kinoshita, Oishi	1937	1565^{III} glass	1.000	36598			36611.6	.137	36609.5	.153

Notes:

[a] Chappuis (1888) used atmospheric nitrogen. In the computation of α, the F values for pure nitrogen were used.

[b] Day and Clement (1908) gave α_0 to four significant figures only.

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Henning and Heuse[5]; and it has been used by the author and his associates with good success.

5. Description of New Measurements of α_v for Nitrogen

In the course of a study[6] of the International and Thermodynamic Temperature Scales from 0 to 450 °C, the thermometric coefficient α_v was determined for nitrogen at five different ice-point pressures with each of two gas thermometers designated by the terms Red and Green. The two vitreous silica bulbs of the gas thermometers and four strain-free platinum resistance thermometers, calibrated[7] in a manner previously described, were placed in a well-stirred oil bath regulated at 0 °C or at 100 °C to ±0.0005 °C. About ten sets of readings at 0 and eight at 100 were taken for each ice-point pressure with each gas thermometer. The

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Table 3. Mean Values of T_0 Determined from the Values of Table 2 Grouped According to (*a*) Gases, (*b*) Publications, (*c*) Laboratories, and (*d*) Dates.

Specification of row	Kelvin temperature of the ice point (T_0 °K)			
	Source of F values used to correct for gas imperfection			
	Keyes	Keesom, Tuyn	Heuse, Otto	Mean of all three
	T_0 °K	T_0 °K	T_0 °K	T_0 °K

(*a*) Mean values of T_0 from the data on the several gases.

Gas	Method	No. of Points				
He	α_v	21	273.180	273.171	273.177	273.176
He	α_p	10	.158	.158	.155	.157
H_2	α_v	19	.144	.136	.138	.139
H_2	α_p	8	.136	.129	.129	.131
N_2	α_v	27	.137	.133	.145	.138
N_2	α_p	15	.140	.139	.152	.143
Ne	α_v	4		.204	.220	.212
Ne	α_p	4		.122	.136	.129

(*b*) Mean values of T_0 from the values of the several publications.

Author	Date	No. of Points				
Chappuis	1888	2	273.121	273.113	273.123	273.119
Onnes, Boudin	1900	1	.127	.115	.119	.120
Chappuis, Harker	1902	4	.105	.102	.111	.106
Travers, Jaquerod	1903	5	.107	.101	.103	.104
Chappuis	1907	6	.119	.111	.122	.117
Day, Clement	1908	4	.192	.188	.199	.193
Holborn, Henning	1911	5	.109	.104	.112	.109
Day, Sosman	1912	1	.085	.082	.090	.086
Henning	1913	1	.190	.182	.184	.185
Eumorfopoulos	1914	5	.157	.156	.167	.160
Chappuis	1917	3	.057	.053	.063	.058
Henning	1921	7	.216	.208	.214	.213
Henning, Heuse	1921	20	.173	.168	.172	.171
Keyes, Townshend, Young	1922	1	.152	.148	.160	.153
Heuse	1926	4		.176	.190	.183
Keesom, v.d. Horst	1927	2	.126	.116	.122	.121
Heuse, Otto	1929	24	.150	.146	.150	.149
Heuse, Otto	1930	2		.130	.146	.138
Keesom, v.d.Horst, Taconis	1933	3	.153	.145	.150	.149
Kinoshita, Oishi	1937	8	.163	.159	.169	.164

(*c*) Mean values of T_0 from the values from the several laboratories.

Laboratory *	Date	No. of Points				
Bureau Int., Paris						
Physical Lab., Leiden						
Univ. College, London						
Geophysical Lab., Washington						
P. T. Reichsanstalt, Berlin						
Mass. Inst. Tech., Cambridge						
Tokio Univ., Tokio						

Table 3.—(*Continued*)

Specification of row	Kelvin temperature of the ice point (T_0 °K)			
	Source of F values used to correct for gas imperfection			
	Keyes	Keesom, Tuyn	Heuse, Otto	Mean of all three
	T_0 °K	T_0 °K	T_0 °K	T_0 °K
(*d*) Mean values of T_0 from the values published during certain periods of time.				
1900 to 1937 (108 points[b])	273.1499	273.1459	273.1529	273.1495
Probable error of mean	0.0032	0.0031	0.0031	
Probable error of single measurement	.0323	.0324	.0325	
1910 to 1937 (86 points)	273.1562	273.1522	273.1588	273.1557
Probable error of mean	0.0036	0.0034	0.0034	
Probable error of single measurement	.0320	.0319	.0316	
1920 to 1937 (71 points)	273.1652	273.1601	273.1662	273.1638
Probable error of mean	0.0035	0.0034	0.0034	
Probable error of single measurement	.0280	.0284	.0283	

Best value from data to 1937: $T_0 = 273.165 \pm 0.015$
$10^7\alpha = 36608 \pm 2$

Notes:

[a] Bureau International des Poids et Mésures: Chappuis, Harker.
Physical Laboratory of Univ. of Leiden: Onnes, Boudin, Keesom, v. d. Horst, Taconis.
University College London: Travers, Jaquerod, Eumorfopoulos.
Geophysical Laboratory of Carnegie Institution: Day, Clement, Sosman.
Physikalisch-Technischen Reichsanstalt: Holborn, Henning, Heuse, Otto.
Massachusetts Institute of Technology: Keyes, Townshend, Young.
Tokio University: Kinoshita, Oishi.

[b] Includes the two points of Chappuis (1888).

results were reduced by use of Equation (4) to idealized conditions and a value of α_v computed for each ice-point pressure. These values are considered in the next section.

6. Determination of the Kelvin Temperature of the Ice Point

From 1900 to 1937, 108 determinations of the thermometric coefficient α_v or α_p were made, and the new measurements mentioned in the previous section give ten more. The gases studied were helium, hydrogen, nitrogen, and neon. A few measurements on argon, carbon dioxide, and air exist but they will not be considered here.

For correcting the 108 determinations for gas imperfections, Equations (37) and (39) were used. Three sets of F_v and F_p values given in Table 1 were employed: (1) those computed from the B values of Professor Keyes, which were derived from a study of all of the available compressibility and Joule-Thomson data; (2) those given by Keesom and Tuyn from a study of the B values at 0 and 100 °C of various investigators, greatest weight having been given the Leiden data; and (3) those given by Heuse and Otto from a formulation of the compressibility data of the Physikalisch-Technischen Reichsanstalt. The results of the reduction of the 108 points are given in Table 2.

In Table 3 these results have been grouped and averaged under the headings: (a) gases, (b) publications, (c) laboratories, and (d) dates. Each value was given unit weight in all averages. The reason for this will appear in the following discussion.

It will be noticed that within the expected error the value of T_0 is independent of the gas or type of thermometer used. The fact that the averages for hydrogen and nitrogen are distinctly smaller than those for helium is explained when one notes that with one exception there are no data on helium before 1920, whereas the early workers contributed many points in the averages for hydrogen and nitrogen; and the early workers obtained low values for T_0. The gas thermometric and compressibility data on neon are at the present time quite meager.

Table 4. Kelvin Temperature of the Ice Point from New M. I. T. Gas Thermometric Measurements on Nitrogen. Corrections for Gas Imperfection by Use of F Values of Other Authors.

The symbols are explained in Table 2.
The values of F_v used are given in Table 1.

p_0 (meters Hg)	$10^7\alpha_v$ °K^{-1}	Ideal gas mean coefficient (α): Kelvin temperature of ice point (T_0)					
		Source of F values used to correct for gas imperfection					
		Keyes		Keesom, Tuyn		Heuse, Otto	
		$10^7\alpha$ °K^{-1}	T_0 °K	$10^7\alpha$ °K^{-1}	T_0 °K	$10^7\alpha$ °K^{-1}	T_0 °K
Red Thermometer							
.99828	36740.48	36608.59	273.1599	36609.41	273.1538	36607.04	273.1715
.74966	36707.01	36607.96	.1646	36608.58	.1600	36606.80	.1733
.59959	36686.30	36607.08	.1712	36607.57	.1675	36606.15	.1781
.44942	36666.57	36607.19	.1704	36607.56	.1676	36606.50	.1755
.33311	36651.84	36607.83	.1656	36608.10	.1636	36607.31	.1695
Mean Red			.1663		.1625		.1736
Green Thermometer							
.99959	36741.18	36609.11	273.1561	36609.93	273.1499	36607.56	273.1676
.75117	36706.89	36607.65	.1669	36608.26	.1624	36606.48	.1757
.60020	36687.50	36608.20	.1628	36608.69	.1592	36607.27	.1698
.45032	36667.80	36608.30	.1621	36608.67	.1593	36607.61	.1672
.33409	36653.27	36609.13	.1559	36609.40	.1539	36608.61	.1598
Mean Green			.1608		.1569		.1680
Mean Red and Green			273.1636		273.1597		273.1708

Grand average $T_0 = 273.1647$

The values of T_0 derived from the measurements given in any one publication are likely to be in fair agreement, no matter what gas was used or whether the gas thermometer was used as a constant-volume or constant-pressure instrument. In gas thermometric measurements it is the systematic rather than the random errors that are large. One of the largest corrections is the dead-space correction which depends on the measurement of the volumes and temperatures of the various parts of the thermometric system not at the bulb temperature; both are difficult quantities to determine. Errors in the thermal expansion of the material of the bulb also introduce a systematic deviation in T_0.

To a remarkable extent the results for T_0 from a single laboratory tend to be uniformly high or low. Probably use of the standardized values for such quantities as the volumes of mercury menisci, the capillary depression, etc., similar

Table 5. Kelvin Temperature of the Ice Point from New M. I. T. Gas Thermometric Measurements on Nitrogen. Correction for Gas Imperfection by Use of F Values Derived from the Measurements Themselves.

The symbols are explained in Table 2.

F_v from smoothed B values	132.55 meters Hg^{-1} °K^{-1}
F_v from unweighted mean slope	132.88
F_v from weighted mean slope	133.40

p_0 (meters Hg)	$10^7\alpha_v$ °K^{-1}	Ideal gas mean coefficient (α): Kelvin temperature of ice point (T_0)					
		Source of F values used to correct for gas imperfection					
		Smoothed B Values		Unweighted mean slope		Weighted mean slope	
		$10^7\alpha$ °K^{-1}	T_0 °K	$10^7\alpha$ °K^{-1}	T_0 °K	$10^7\alpha$ °K^{-1}	T_0 °K
Red Thermometer							
.99828	36740.48	36608.16	273.1631	36607.83	273.1656	36607.31	273.1695
.74966	36707.01	36607.64	.1670	36607.40	.1688	36607.01	.1717
.59959	36686.30	36606.82	.1731	36606.63	.1746	36606.31	.1769
.44942	36666.57	36607.00	.1718	36606.85	.1729	36606.62	.1746
.33311	36651.84	36607.69	.1666	36607.58	.1675	36607.40	.1688
Mean Red			.1683		.1699		.1723
Green Thermometer							
.99959	36741.18	36608.68	273.1593	36608.35	273.1617	36607.83	273.1656
.75117	36706.89	36607.32	.1694	36607.07	.1713	36606.68	.1742
.60020	36687.50	36607.94	.1648	36607.75	.1662	36607.43	.1686
.45032	36667.80	36608.11	.1635	36607.96	.1646	36607.73	.1664
.33409	36653.27	36608.99	.1569	36608.88	.1578	36608.70	.1591
Mean Green			.1628		.1643		.1668
Mean Red and Green			273.1656		273.1671		273.1695

Grand average $T_0 = 273.1674$

methods of calibration, and similar methods of reduction of the observations by all workers in the same laboratory tend to introduce systematic deviations.

The most interesting averages of Table 3 are those for periods of time. As the older data are discarded, the value of T_0 increases. It should be remembered that in all cases the measurements of the thermometric coefficients before 1920 were taken not for the determination of the values of the coefficients themselves but for the purpose of determining thermodynamic temperature, usually high or low temperatures. The measurements since 1920 (except those of Henning, 1920, and Keyes, Townshend, and Young, 1922) were made solely for the purpose of determining T_0, and the gas thermometer systems were designed to obtain maximum accuracy in the determination of the thermometric coefficient.

Hence, I select as the best values of α and T_0 from the data of 1900 to 1937 the mean of all measurements from 1920 to 1937:

$$10^7\alpha = 36608 \pm 2\ °\mathrm{K}^{-1};\quad T_0 = 273.165 \pm 0.015\ °\mathrm{K}.$$

It is interesting to note that Heuse and Otto (see Table 7) select from the work of the P. T. R. the same value for α, but round off its reciprocal 273.1643 to 273.16.

In Table 4 the new data on nitrogen are treated in a manner similar to that employed for the data of other authors in Table 2. The mean value of T_0 obtained in this way is 273.1647. In Table 5 the new data on nitrogen are reduced by use of (1) the B values derived from the new gas thermometric data on nitrogen from 0 to 450 °C, which have been smoothed analytically; (2) the mean slope, F_v, of α_v from the Red and Green thermometers fitted by the equation

$$\alpha_v = \alpha + F_v p_0$$

by the method of least squares, each value of α_v being given unit weight; and (3) the mean slope determined with the six values of α_v for $p_0 = 1000$, 600, and 450, given the weight of two measurements, the other four being given the weight of one measurement, this being done as a result of a statistical treatment of all of the primary data. The mean value, T_0, from such a treatment of the results is 273.1674.

Table 6. Selected Values of the Kelvin Temperature of the Ice Point as of 1939.

Source	No of Points	T_0 °K
From all data 1920–1937 (Table 3)	71	273.165
From M. I. T. 1939 data (Table 4)	10	273.165
From M. I. T. 1939 data (Table 5)	10	273.167

Recommended values: $T_0 = 273.165 \pm 0.015$ °K
$10^7 \alpha = 36608 \pm 2$ °K^{-1}

In Table 6 the results of all the measurements are summarized. The best representative value of T_0 is 273.165 ± 0.015.

In Table 7 is given a summary of the values of α and T_0 selected by other authors and those selected as a result of the present treatment of all of the gas thermometer data. I select as the best values:

$$10^7\alpha = 36608 \pm 2 \text{ °K}^{-1}; \quad T_0 = 273.165 \pm 0.015 \text{ °K}.$$

From Birge's [8] values of RT_0—$(22.4141 \pm 0.0008) \times 10^3$ cm^3 atm. mole^{-1} and 22.4135 ± 0.0008 liter atm. mole^{-1} at standard gravity (980.665 dyne gram^{-1})—and the foregoing value of T_0, we obtain for the universal gas constant R:

$$R = 82.053 \pm 0.005 \text{ cm.}^3 \text{ atm. mole}^{-1} \text{ °K}^{-1}$$
$$R = (82.051 \pm 0.005) \times 10^{-3} \text{ liter atm. mole}^{-1} \text{ °K}^{-1}$$

7. Summary

The theory of the correction of the observations made on constant-volume and constant-pressure gas thermometers for deviation of the actual from the experimental instrument is outlined. The three methods of correction of the thermometric coefficients α_v and α_p for gas imperfection are given in detail. From a consideration of all of the gas thermometric data available the values of the thermometric coefficient α of an ideal gas and of the Kelvin temperature T_0 of the ice point selected as the best at the present time are:

$$10^7\alpha = 36608 \pm 2 \text{ °K}^{-1}; \quad T_0 = 273{,}165 \pm 0.015 \text{ °K}.$$

With Birge's values of RT_0, the values above give:

$$R = 82.053 \pm 0.005 \text{ cm.}^3 \text{ atm. mole}^{-1} \text{ °K}^{-1}$$
$$R = (82.051 \pm 0.005) \times 10^{-3} \text{ liter atm. mole}^{-1} \text{ °K}^{-1}$$

for standard gravity.

Table 7. Values of the Kelvin Temperature of the Ice Point Selected by Several Authors.

Date	$10^7\alpha$ °K^{-1}	T_0 °K	Author	Gases Considered	Data Used for Correction
1903		273.10	Callendar [1]	H_2	Joule-Thomson
1904		273.09	Berthelot [2]	H_2, CO_2, Air	Compressibility
1907		273.08	Berthelot [2]	H_2, N_2, CO_2, Air	Compressibility
1907		273.17[a]	Buckingham [3]	H_2, N_2, CO_2, Air	Joule-Thomson
1907	36617	273.10	Onnes, Braak [4]	H_2	Compressibility
1908		273.13	Rose-Innes [5]	H_2, N_2	Joule-Thomson
1915		273.09[b]	Henning [6]		
1920		273.14	Keyes [7]	He, H_2, N_2	Compressibility
1921, 1926	36604	273.20[e]	Henning, Heuse [8]	He, H_2, N_2	Compressibility
1922		273.10 ± 0.05[b]	Day, Sosman [9]		
1923		273.13 ± 0.01	Smith, Taylor [10]	N_2	Compressibility
1924	36615	273.11	Keesom, Onnes [11]	He, H_2, N_2	Compressibility
1925		273.15[d]	Roebuck [12]	Air	Joule-Thomson
1926		273.20[c]	Henning [13]	He, H_2, N_2	Compressibility
1926		273.1[b]	I. C. T. [14]		
1929		273.18 ± 0.03[b]	Birge [15]		
1929	36610	273.15	Otto [16]	He, H_2, N_2, Ne	Compressibility
1929		273.14 ± 0.01	Schames [17]	He, H_2, N_2	Compressibility
1929, 1930	36608	273.16[c]	Heuse, Otto, Henning [18]	He, H_2, N_2, Ne	Compressibility
1936	36610	273.15[e]	Keesom, Tuyn [19]	He, H_2, N_2, Ne	Compressibility
1936		273.16 ± 0.02	Roebuck [20]	He, N_2, Air	Joule-Thomson
1939		273.16 ± 0.02[b]	Wensel [21]		
1939	36608	273.165 ± 0.015	Beattie	He, H_2, N_2, Ne	Both types

Notes:

[a] Buckingham averaged his value with those of Berthelot and proposed 273.13 as the best value.

[b] These values were derived from a consideration of those proposed by other authors, not from a reconsideration of gas thermometry data.

[c] These values were derived from the data of the Physikalisch-Technischen Reichsanstalt alone.

[d] From a reformulation of the data used by Roebuck, F. G. Keyes [22] obtained the value 273.135.

[e] This value rests almost entirely on the Leiden data for helium.

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Slopes of the *pv* Isotherms of Some Thermometric Gases at Pressures Below Two Atmospheres

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1. Introduction

In many fields of science it is frequently possible to calculate a desired result in several different ways, sometimes employing the results of more than one set of measurements. In many cases, it is found that such calculations lead to somewhat different results, depending upon the assumptions and auxiliary numerical values used to obtain a derived result. If great exactness is desired it is obvious that careful consideration should be given to the reliability of (1) each set of experimental data, (2) each result derived therefrom, (3) the various methods of calculation and (4) the assumptions employed. This appears to be especially applicable to the derivation of some of the so-called fundamental or basic physical constants, which cannot be obtained by direct measurement but must be obtained indirectly by calculation using certain assumptions.

The numerical values of many basic physical constants which have been used for years are now in such an unsettled state that it is difficult for an unbiased person to decide which of the many published "recommended" or "accepted" values to use in his calculations. While this is particularly true in the case of the so-called atomic constants, it also appears to apply to what may be called thermodynamic constants, including the gas constant (R,k) the absolute temperature of certain "fixed points," such as the ice point, and the atomic or molecular weights of some of the simpler gases.

It is not the intention in this paper to derive additional "recommended" or "accepted" values for these constants but rather (1) to examine the reliability of some of the experimental data and methods used to obtain derived values for such constants, (2) to follow some of the recommended procedures which have proved useful in the appraisal of experimental data, and (3) to point out some of the apparent misinterpretations, inconsistencies and discrepancies existing in the data on the properties of certain gases at pressures below two atmospheres.

2. Available Data

There are available in the literature and in physical and chemical tables and handbooks very extensive data on the density or specific volume of different gases at various pressures and temperatures, often referred to as p,v,T data. Many of these published data are supposed to be the direct result of experiment and are frequently given in non-integral multiples of some unit of density or specific volume, pressure and temperature. Comparison of the experimental results of one observer with those of another observer which are expressed in different non-integral multiples of a different set of units, can be made accurately in general only by the expenditure of considerable arithmetical labor and by employing reliable methods of interpolation. Some data, which are given at integral temperatures and pressures, are supposed to be results obtained from experiments by some process of smoothing, the details of which are usually not specified. In some cases, the results of a certain set of experiments, such as those obtained at a constant temperature, are given in the form of an empirical equation. In other cases, a large group of experimental results covering a range of both temperature and pressure is embodied in a single equation, frequently called an equation of state. Many different forms of such equations with various degrees of complexity have been devised, but it is rather significant that there has been a pronounced decline in the number of such equations published in the last decade.

While it is possible to calculate from such equations not only the slopes of the pv isotherms but also many other important characteristics of gases, a serious difficulty arises if the demands as to accuracy are high, and if careful consideration is given to the reliability of such derived results. In many instances the situation is so complex that it is exceedingly difficult, or next to impossible, to make even an educated guess as to the reliability of a derived result.

A superficial examination of the isothermal pv data discloses that the experimental results of the different observers in the range below two atmospheres generally differ markedly. Further investigation discloses that the results derived from a given set of experiments, including observations above this range and also at about one atmosphere pressure, differ appreciably depending upon the interpretation of the experimental data and the methods employed to obtain a derived result.

There appear to be two schools of thought relative to the best method of determining numerical values for the slopes of the pv isotherms below two atmospheres. One group of experimenters, working in the field of atomic and molecular weights, uses only data obtained at and below one atmosphere pressure in the reduction of their data, completely ignoring the existence of data at higher pressures. The propriety of this procedure has been questioned by Wild.[1] In obtaining probable values for certain atomic weights and also the gas constant, R, Birge[2] identifies himself with this school by ignoring data above one atmosphere.

Another group of experimenters, working in the field of gas thermometry, makes similar reductions of their results obtained at pressures below two atmospheres, but uses values for the isothermal slopes deduced from pressures considerably above this range. The Physikalisch-Technische Reichsanstalt and the Leiden laboratory have published extensive data obtained in the interval 1 to 100 atmospheres. Since the major use they have made of these data is in the reduction of their gas thermometry results, their position on the subject may be inferred.

Since both groups have one point in common, namely, at one atmosphere which has been used almost universally as a conventional reference point, it appeared to be worthwhile to examine the course of the pv curve on both sides of this reference point using some of the most precise data obtained by each group. It is generally assumed by both groups that the pv versus p, or the pv versus $\frac{1}{v}$ curves are straight lines below two atmospheres within the experimental errors of the measurements. For the purpose of this paper, the slopes of these curves are regarded as important quantities whose numerical values are needed to the highest accuracy attainable for calculating other important derived physical constants.

3. Theoretical Predictions

While the approach here is chiefly from the experimental side, it may be well to summarize briefly some of the predictions of theory, especially those relating to the form of equation which may be expected to represent experimental results satisfactorily. One important prediction is that at 0 °C, at least, no chemical changes such as dissociation and association are to be expected in the case of the simpler monatomic and diatomic gases. Another is that the pressure, p, is a function only of the density, ρ, for a given kind of gas at a fixed temperature. Suppose it is assumed that the function is a power series

$$p = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\ldots\ldots \tag{3.1}$$

which is known to be capable of representing any curve if enough terms are employed. Suppose further that the constant coefficients, the a's, are determined from experimental data, using the method of least squares. Theory demands that $a_0 = 0$, but it practically never turns out to be zero identically in a least squares treatment of the experimental data. It is very generally agreed that this may easily be ascribed to experimental errors and that the series may be written

$$pv = \frac{p}{\rho} = a_1 + a_2\rho + a_3\rho^2 + \tag{3.2}$$

where v is specific volume. It should be noted that pv has the physical dimensions of energy per unit mass which makes it an important parameter from the standpoint of thermodynamics and statistical theory, which employ the well-known exact laws of conservation of mass and energy and permit the adding up of separate contributions to the total energy. Statistical theory predicts that at low pressures the foregoing series should be mathematically convergent, so that each succeeding term must be smaller than the preceding term.

All of these theoretical predictions appear to be amply supported by experiment. That the series is rapidly convergent is clearly indicated by the numerical values obtained from experiments which are considered later. For He, Ne, A, H_2, N_2 and O_2 at 0 °C and one atmosphere, for example, the term $a_2\rho$ turns out to be less than 0.1 per cent of a_1 in all cases, and the term $a_3\rho^2$ is at most of the order of a few parts in a million compared to a_1.

It is common practice to reduce pv measurements at pressures where high accuracy is attainable to low-pressure conditions, in much the same way that accurate weighings are reduced to so-called vacuum conditions, that is, to what would have been obtained if the measurements had been made at very low pressures. The fact that accurate measurements cannot be made at low values of p and ρ appears in principle to be of no more practical importance than the fact that accurate weighings cannot be made in an absolute vacuum.

At very low pressures Equation (3.2) reduces to a form which embodies the laws of ideal or perfect gases given in many textbooks, namely

$$pv = \frac{RT}{M} = a_1 \tag{3.3}$$

where R is the universal gas constant, T is absolute temperature and M is molecular weight, all three being determinable from combinations of experimental values for a_1.

Modern theories attribute the known deviations from the foregoing equation to the mutual interaction of the gaseous particles, sometimes referred to as van der Waals' forces. It is generally agreed that the force of attraction between two such particles varies inversely as r^6, where r is the distance between centers. In some instances the force of repulsion is assumed to vary inversely as r^n where n is about 9 to 12; in other instances an exponential relation is assumed. In any case, it seems clear that as the density is decreased indefinitely, the frequency of collisions, using the language of kinetic theory, must decrease. Since the average distance apart also decreases, the effects of Van der Waals' forces must also decrease, yielding values for a_1 at very low pressures which are independent of such effects, often called imperfections of the gases.

The situation at present, relative to the specific effects of such imperfections, appears to be that theory is not yet far enough advanced to predict reliable values for the constant a_2 and that better experimental values are needed in order to test adequately various hypotheses and to aid in the development of reliable theories.

4. Methods of Calculation

An accurate value for a_2, which has a different value for every temperature, has been the major goal of many valuable experimental investigations. Some of the methods used to calculate a_2 from a given set of measurements, particularly at higher pressures, are open to several serious objections, because inaccuracies in a_2 have been introduced thereby which appear to exceed the inaccuracies inherent in the measurements themselves. High accuracy in calculations of this kind, as in the measurements, can be obtained only by exercising eternal vigilance in a multiplicity of small details. Many of these details appear worthy of brief mention here since they are ignored by many workers in this field.

It seems to be generally agreed that least squares methods yield the "best" results and at the same time furnish an impersonal method of calculating mathematical probable errors which may be attached to published data. There are in the present application what may be termed chemical errors, introduced by the presence of impurities in the gases, and also physical errors, introduced in the calibration of weights and of the instruments used to measure pressure in terms of the fundamental standards of mass, length and time, as well as many other possible physical sources of error. The true probable error should include all three kinds of errors, but the chemical and physical errors cannot be evaluated adequately in general from published information. Only by comparison of results from several independent investigations which differ by more than the sum of their mathematical probable errors can evidence be obtained of the magnitude of the other errors.

Least squares methods have been followed here, but as pointed out by Birge[2] some judgment must be used in particular applications. For example, many of the results from the atomic weight group give densities at only three pressures. If three terms in Equation (3.2) are used, the fit is exact. If only two terms are used and each measurement is given equal weight, the usual solution yields the best simultaneous set of values for a_1 and a_2. From the standpoint of atomic weights, the emphasis is on obtaining a_1, but the immediate emphasis here is on obtaining the best value of a_2 from the measurements.

Considerable arithmetical labor may be saved by choosing one point as a reference and eliminating a_1. While any point might be chosen in principle, one atmosphere and 0 °C has been used for convenience and designated by the subscript zero throughout this paper, unless otherwise specifically stated. Thus, writing the equation for any corresponding values of p and ρ

$$pv = a_1 + a_2\rho$$

and for the reference point

$$p_0v_0 = a_1 + a_2\rho_0$$

Elimination of a_1 gives

$$pv - p_0v_0 = a_2\rho - a_2\rho_0 \quad \text{or} \quad \frac{pv - p_0v_0}{\rho - \rho_0} = a_2 \tag{4.0}$$

The mean value of a_2 obtained by this method of calculation is the same as the one obtained by the previous method, if each point is again given equal weight. In this form, however, judgment and appreciation of errors of measurements dictate that two points close together are not entitled to the same weight as two points far apart. A fairer method of weighting seems to be to assign weights proportional to the distance apart, or more precisely to weight each value of a_2 in proportion to the denominator of Equation (4.0) in obtaining the mean value of a_2. This method has been used here in several instances and the calculated probable error has been materially reduced by so doing.

Thus far no attention has been given to the question of dimensions and units. It is obvious that $a_2\rho$ must have the same dimensions as pv; hence the numerical value of a_2 depends upon the units used. The very large number of different units used to express p, v and ρ make inter-conversions for different combinations of units very difficult and troublesome at times. Such difficulties may be easily eliminated by writing the equation in the equivalent forms

$$pv = p_0v_0\left[1 + a_2'\left(\frac{\rho}{\rho_0} - 1\right)\right] \qquad \frac{\dfrac{pv}{p_0v_0} - 1}{\dfrac{\rho}{\rho_0} - 1} = a_2'$$

in which a_2' is obviously dimensionless and independent of the units used for p, v and ρ.

In many cases the density is not measured. The mass of gas is held constant and only the volume is measured, so that $\frac{\rho}{\rho_0}$ must be replaced by $\frac{v_0}{v}$. Similarly, for convenience, $\frac{\rho}{\rho_0}$ is very frequently replaced by $\frac{p}{p_0}$, which involves an approximation good to better than 0.1 per cent in most cases considered here below two atmospheres, which is better than a_2 is known in general. Another alteration sometimes made is the use of an exponential equation. Since $e^x = 1 + x + \frac{x^2}{2} + \ldots\ldots$, with $x = a_2'\left(\frac{\rho}{\rho_0} - 1\right)$ which is here always less than 0.001 below two atmospheres, $\frac{x^2}{2}$ and higher power terms are less than 1 in 10^6. None of the measurements of p or v appears to be reliable to better than this amount.

These several alterations are referred to later so that the various forms are assembled here as

$$pv = p_0v_0\left[1 + \alpha_1\left(\frac{v_0}{v} - 1\right)\right] \qquad \frac{\dfrac{pv}{p_0v_0} - 1}{\dfrac{v_0}{v}} = \alpha_1 \tag{4.1}$$

$$pv = p_0v_0e^{a_2\left(\frac{v_0}{v} - 1\right)} \qquad \frac{\ln \dfrac{pv}{}}{\dfrac{v_0}{v} - 1} \tag{4.2}$$

$$pv = p_0v_0\left[1 + \alpha_3\left(\frac{p}{p_0} - 1\right)\right] \quad \text{or} \quad \frac{\dfrac{}{p_0v_0} - 1}{\dfrac{p}{p_0} - 1} = \alpha_3 \tag{4.3}$$

$$pv = p_0v_0e^{\alpha_4\left(\frac{p}{p_0} - 1\right)} \quad \text{or} \quad \frac{\ln \dfrac{pv}{p_0v_0}}{\dfrac{p}{p_0} - 1} = \alpha_4 \tag{4.4}$$

The symbol α, with a different subscript for each form of equation, is used to denote that they are not identical in value but for practical purposes they are all the same as a_2' in the range below two atmospheres. In precise language, each α represents a number obtained from measurements at any equilibrium state (pv) and at the reference state (p_0v_0) on a constant mass of gas at a constant temperature. In this sense the α's differ from the constant coefficient a_2 in that they are variable coefficients analogous to the α in the familiar equation $l = l_0 [1 + \alpha (t - t_0)]$ in which l is length, t is temperature and α is usually called the coefficient of linear expansion. Over a short interval all α's may be considered as constants for practical purposes, but measurements made over a wide interval prove them to be variables in every case. The fact that Equations (4.1) to (4.4) all reduce to $\frac{0}{0} = \alpha$ at the reference state is of no consequence, for differentiation of these equations shows that all α's represent the derivative at this point, and hence they replace in the more exact mathematical language what have previously been called the isothermal pv slopes.

The analogy between the pv coefficients and the coefficient of linear expansion appears to be very close in several respects. For example, judgment dictates that a highly reliable value for the coefficient of expansion of steel or fused silica cannot be obtained by making measurements with attainable precision at two temperatures one degree apart. The pv coefficients are correspondingly small and judgment again dictates that reliable values cannot be expected from measurements with attainable precision at pressures one atmosphere or less apart. In both cases it appears that greater reliability may be obtained by representing α, obtained from measurements over a wide interval, by means of an adequate empirical equation and then calculating therefrom a value of α at the reference point, which very probably would have been obtained if more precise measurements could have been made in the immediate vicinity of the reference point.

5. Uncertainties

The major objective here is to obtain not only a value for a_2 or α at one atmosphere from different investigations but also an estimate of reliability. In most investigations there are only a few, usually 3 to 8, essentially different points which serve to define a curve. The calculated value for the slope of the curve at one atmosphere may be so materially affected by systematic errors and by the form of analytical relation assumed to represent the curve that the calculated probable error may have but little significance as a criterion of reliability, and may give a false sense of security in the particular application. In order to make some allowance, although arbitrary, for such effects, the estimated uncertainty has been taken as approximately 3 times the mathematical probable error, following in general the recommendations of Rossini and Deming.[3]

There are only two types of application used here. When α is assumed to be constant over an interval within the indicated precision of the data, the uncertainty, u, in the mean value of α is taken as

$$u = 2\left[\frac{\Sigma w\Delta^2}{(n-1)(\Sigma w)}\right]^{\frac{1}{2}} \tag{5.1}$$

When a linear relation such as $\alpha = a + bx$ is assumed, the uncertainty in a or the value of α when $x = 0$, obtained by the method of least squares, is taken as

$$u = \frac{2}{(n-2)^{\frac{1}{2}}}\left[\frac{(\Sigma w\Delta^2)(\Sigma wx^2)}{(\Sigma wx)^2 - (\Sigma w)(\Sigma wx^2)}\right]^{\frac{1}{2}} \tag{5.2}$$

In both cases, n is the number of observations, w is the weight assigned and Δ is the residual or difference between the observed and calculated value of α.

An estimate of the true but unknown uncertainty may be obtained by assigning errors to each element which enters into the final result. In most of the measurements it appears almost certain that the true errors in each element are less than 1 in 10^3. Hence, to an approximation good to better than 1 in 10^6, the error in pressure may be written

$$p' = p + \Delta p = p\left(1 + \frac{\Delta p}{p}\right) = pe^{\frac{\Delta p}{p}} \tag{5.3}$$

where p' is the true value, p is the observed value, Δp is the true error and $\Delta p/p$ is the fractional error in p. Similar relations may be written for volume, v, mass, m, and temperature, T, so that

$$\frac{p'v'}{p_0'v_0'} = \frac{pv}{p_0v_0}e^y \tag{5.4}$$

where the combined fractional errors are

$$y = \frac{\Delta p}{p} - \frac{\Delta p_0}{p_0} + \frac{\Delta v}{v} - \frac{\Delta v_0}{v_0} + \frac{\Delta m}{m} + \frac{\Delta T}{T} \tag{5.5}$$

which includes possible errors in the assumed constancy of mass and temperature. Thus, the true error in α appears in the last terms of relations, such as

$$\frac{\ln\frac{p'v'}{p_0'v_0'}}{\frac{p'}{p_0'} - 1} = \frac{\ln\frac{pv}{p_0v_0}}{\frac{p}{p_0} - 1} + \frac{y}{\frac{p}{p_0} - 1} \quad \text{or} \quad \alpha_4' = \alpha_4 + \frac{y}{\frac{p}{p_0} - 1} \tag{5.6}$$

$$\frac{\frac{p'v'}{p_0'v_0'} - 1}{\frac{p'}{p_0'} - 1} = \frac{\frac{pv}{p_0v_0} - 1}{\frac{p}{p_0} - 1} + \frac{\frac{pv}{p_0v_0}y}{\frac{p}{p_0} - 1} + \ldots \quad \text{or} \quad \alpha_3' = \alpha_3 + \frac{\frac{pv}{p_0v_0}y}{\frac{p}{p_0} - 1} + \ldots \tag{5.7}$$

and corresponding relations for α_1 and α_2 with $\left(\frac{v_0}{v} - 1\right)$ in the denominator. The error in the denominator has been neglected for simplicity, since by hypothesis this affects α less than 1 in 10^3, while the last term may be many times this amount.

For oxygen and argon, α is of the order of 10^{-3}. In order to obtain a value of α for oxygen or argon with a true uncertainty of less than one per cent, the combined fractional errors, y, must be less than the following:

$\frac{p}{p_0} - 1$	y
0.5	5×10^{-6}
1	10^{-5}
10	10^{-4}
100	10^{-3}

For the other gases included herein, α is about 4 to 6×10^{-4} so that the corresponding requirements are only slightly higher.

The scatter of the computed values of α obtained from measurements at less than 2 atmospheres indicates random fractional errors of several units in 10^{-5}, even in the most precise measurements available, and very much larger errors in other cases which it has not seemed worthwhile to consider in detail here. Since there is no positive assurance that the systematic errors may not be as large as or even larger than the apparent random errors, which already exceed the limits stated above, it is obvious that α cannot be obtained with a true uncertainty of less than one per cent from available measurements at pressures less than 2 atmospheres.

With measurements over an interval of 10 atmospheres or more the requirements are obviously not so exacting. It appears that the combined fractional errors in some of the published measurements at high pressures may not exceed about 10^{-4} in several instances. One of the uncertainties in the values for α at one atmosphere obtained from measurements over a large pressure interval appears to be in the analytical relations used to represent α over such an interval. In several instances linear relations have been used, whereas the data clearly indicate that such a relation is inadequate. A constant error obviously introduces an erroneous apparent trend in the values of α. Hence, anomalous trends in the values of α may well be viewed with suspicion and interpreted as possible evidence of the presence of systematic errors. In some instances the variation of α with pressure is small, for example, a few units in 10^{-8} per atmosphere for helium. There appears to be little reason for doubting that the values of α for helium at 0 °C and low pressures, obtained from measurements over a wide pressure interval, are much more reliable than the values obtained from any available measurements over a small pressure interval at low pressures.

In view of the fact that small errors of the order of 10^{-5} and less become significant in some instances, it may be pointed out that the method of calculation using ratios automatically eliminates the effect of some of the possible systematic errors of this magnitude. For example, where p and p_0 are both measured by means of a mercury manometer

$$\frac{p}{p_0} = \frac{\rho h g}{\rho_0 h_0 g} \qquad (5.8)$$

where ρ is the density of mercury, h is the height of mercury column and g is the average gravitational acceleration at the place where p is measured. The absolute value of g is obviously eliminated and the absolute values of density are not needed as long as the density is uniform and proper corrections for temperature and pressure are applied. Thus, the uncertainty in the ratio $\frac{p}{p_0}$ reduces essentially to uncertainties in the measurements of h, except for capillarity corrections and other small but sometimes appreciable corrections, such as for gas columns.

The case is different, however, when p_0 is measured with a mercury manometer and p is measured with a piston gauge. In this case

$$\frac{p}{p_0} = \frac{mg/A}{\rho_0 h_0 g} \qquad (5.8)$$

where A is the effective area of the piston and m is the effective mass of the piston and weights applied. The absolute value of g is eliminated, but uncertainties in the absolute values of all the other factors are involved. Thus, an important element is the calibration of the piston gauge, which is usually done by comparison with a mercury manometer; but many of the details of such calibrations are frequently not published. The agreement of results from different laboratories in several instances supplies indirect evidence that uncertainties in such calibrations apparently do not exceed about 10^{-4}.

Pressures much above one atmosphere are frequently determined at the Leiden laboratory by means of closed-end manometers which are usually filled with hydrogen. In Leiden Communication No. 227a (1933), it is stated that in order to obtain a precision of 10^{-4} several improvements in the calibration and temperature control of the closed-end manometers were necessary. In a footnote, 1.35 mm is given as the radius of the tube containing the mercury meniscus. Uncertainties are recognized in the capillary corrections which are relatively large in a tube of this size. There are also uncertainties in the volume of the gas beneath a plane tangent to the mercury surface, since the meniscus may assume various heights and shapes for a given setting of the vertex.

Illustrations are given later of other uncertainties which, for one reason or another, have found their way into some of the published values for α at low pressures. Many of the calculations of $\frac{pv}{p_0v_0}$ and α have been carried to one place beyond those given in the original publications in order to obtain adequate values of u in Equations (5.1) and (5.2) and to minimize uncertainties in the calculations themselves.

6. Oxygen

While the Reichsanstalt measurements include a number of gases and appear to be in reasonably good agreement with measurements obtained in other laboratories, all the analytical relations published as representations of the measurements appear to be somewhat erroneous. Since the reason for this unfortunate state of affairs is the same for all the gases and has not been pointed out previously, the data on oxygen are discussed in some detail as an illustration.

Referring to the data given in any horizontal row in Table 1, the measurements were obtained essentially as follows: a pressure (column 1) is measured by means of a piston gauge; a valve is closed, confining an unmeasured mass of gas in a known volume (column 2); another valve is opened, permitting the same mass of gas to expand into another known volume (column 4); and the pressure (column 3) is measured at approximately one atmosphere with a mercury manometer. The data in column 5, which were calculated from the data in the previous four columns, were used by Holborn and Otto to derive the following equation:*

$$pv = 1.00130 - 1.30143 \times 10^{-3}p + 3.68981 \times 10^{-6}p^2 \qquad (6.1)$$

where p is in m Hg and $v = 1$ when $p = 1$. This equation, transformed to the form used here with 0 °C and one atmosphere as the reference state, becomes

$$\frac{pv}{p_0v_0} = 1 - 98.451 \times 10^{-5}\left(\frac{p}{p_0} - 1\right) + 2.13056 \times 10^{-6}\left(\frac{p}{p_0} - 1\right)^2 \qquad (6.2)$$

Equation (6.1) was apparently derived so as to reduce to $pv = 1$ when $p = 1$ m Hg, but the data in column 5 are obviously not on this basis. As a matter of fact each row of data in the first five columns applies to a particular mass of gas and the different rows are not on a comparable basis. Adding to the data in column 5 the corrections in column 6 yields the data in column 7 which are all on the same basis. The corrections are relatively small since p_0 observed is not far from

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* Attention is called to the fact that the values of c in the equations $pv = a + bp + cp^2$ for oxygen at 0, 50 and 100 °C given in *Z. Physik*, **10**, 371, 1922, are in error. Corrected values for c are given in a later summary, *Z. Physik*, **33**, 6, 1925, which contains the equation quoted here.

Table 1. Data on Oxygen at 0 °C and 1 to 100 Atmospheres Obtained by Holborn and Otto.

p mm Hg (1)	v ml (2)	p_0 mm Hg (3)	v_0 ml (4)	Observed $\frac{pv}{p_0v_0}$ (5)	Correction to $p_0=760$ (6)	Corrected $\frac{pv}{p_0v_0}$ (7)	Corrected $\frac{pv}{p_0v_0}$ (8)	$\frac{p}{p_0}$ (9)	$\frac{v_0}{v}$ (10)	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	Mean Values $-10^4\alpha_1$	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{p}{p_0}-1}$	Mean Values $-10^4\alpha_2$
18960.1	106.025	775.06	2651.28	0.978268	-19×10^{-6}	0.978249	0.97798	24.9475	25.5022	8.8772		9.0828	
18995.0	106.024	776.63	2651.32	.978064	−21	.978043	.97778	24.9934	25.5545	8.9425	8.9415	9.1513	9.1506
19055.5	106.023	780.60	2646.83	.977836	−26	.977810	.97754	25.0735	25.6425	9.0048		9.2176	
37788.1	106.016	811.42	5157.09	.957362	−64	.957298	.95706	49.7212	51.9392	8.3829	8.3858	8.7646	8.7680
37811.0	106.015	813.90	5144.74	.957306	−67	.957239	.95701	49.7513	51.9737	8.3888		8.7713	
56045.1	106.005	766.73	8246.73	.939593	−8	.939585	.93930	73.7436	78.4853	7.7970	7.7670	8.3053	8.2922
56098.2	106.006	766.79	8252.82	.939725	−9	.939716	.93943	73.8134	78.5486	7.7371		8.2729	
74849.0	105.998	798.74	10741.62	.924716	−48	.924668	.92442	98.4855	106.5090	7.1399	7.1331	7.7275	7.7220
75394.8	105.998	804.99	10741.04	.924277	−56	.924221	.92398	99.2037	107.3376	7.1263		7.7165	

In Fig. 1 the coördinates of the points for oxygen on curves 2 and 3 are:

2 3 3 2

Columns (1), (2), (3), and (4) Observed values quoted from *Z. Physik*, 10, 367 (1922).

Column (5) Calculated from observed values.

Column (6) Based on $\alpha = \frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t = -9.5 \times 10^{-4}$.

Column (7) Corrected to common reference state, $p_0 = 760$ mm Hg, from values in columns (5) and (6).

Column (8) Values quoted from "Handbuch der Experimental Physik," 8 (2), p. 175, with one atmosphere as the reference state.

Column (9) Obtained from data in column (1) by dividing by $p_0 = 760$ mm Hg.

Column (10) Obtained by dividing data in column (9) by data in column (7).

760 mm. In other instances, p_0 observed ranged from less than 500 mm to over 900 mm, and the corrections are larger. Applications of these necessary corrections materially improves the general consistency of the Reichsanstalt measurements.

Holborn and Otto have evidently misinterpreted all their measurements as having 1 m Hg and 0 °C as the reference state, possibly because p in m Hg was used for convenience in the equations. Further evidence of this misinterpretation is supplied by the values in column 8 which are given by Otto in the "Handbuch der Experimental Physik." Apparently these values were obtained from column 5, misinterpreted as on a 1 m Hg basis, and corrected to a 760 mm Hg basis. The effect of this misinterpretation is shown graphically in Fig. 1. The dashed line 1 at the top, representing Equation (6.2), is obviously a very poor representation of the observed points and consequently yields an erroneous value of α at one atmosphere.

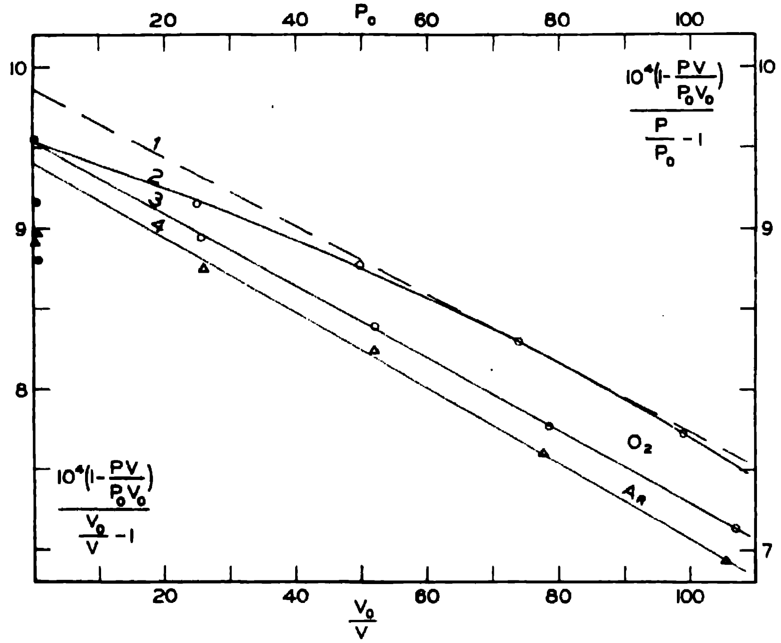

FIG. 1. Data on oxygen (circles) and argon (triangles) at 0 °C; Reichsanstalt data at 25 to 100 atmospheres; Baxter and Starkweather data below one atmosphere. Coördinates of lines 1 and 2 at top and right; coördinates of lines 3 and 4 at bottom and left. Line 1 represents Equation (6.2); line 2 represents α_s as a quadratic function of p/p_0. Line 3 represents Equation (6.3) for oxygen. Line 4 represents Equation (7.1) for argon.

Curve 2 in Fig. 1 indicates clearly that the observed values of α_3 given in Table 1 cannot be represented adequately by a straight line. On the other hand, line 3 indicates that it represents reasonably well the observed values of α_1 in Table 1. The weighted least squares equation for line 3 is

$$\frac{pv}{p_0v_0} = 1 - (95.13 \pm 0.94) \times 10^{-6}\left(\frac{v_0}{v} - 1\right) + 2.246 \times 10^{-8}\left(\frac{v_0}{v} - 1\right)^2 \qquad (6.3)$$

The values of α obtained from measurements below one atmosphere by Baxter and Starkweather, considered later, have been included in Fig. 1 to indicate that they appear inconsistent with the Reichsanstalt measurements, as might be expected from the previous discussion on uncertainties.

Table 2. Data on Oxygen at 0 °C and 1 to 55 Atmospheres Obtained by Van Urk and Nijhoff.

$\frac{p}{p_0}$ (1)	(2)	p_0v_0 (3)	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$ (4)	$0.2246\left(\frac{v_0}{v}-1\right)$ (5)	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$ (6)
36.20	37.38	0.9685	86.6	8.1	94.7
38.77	40.13	.9661	86.7	8.8	95.5
46.90	48.91	.9590	85.6	10.8	96.4
47.15	49.17	.9589	85.4	10.8	96.2
54.75	57.45	.9528	83.6	12.7	96.3
					Mean = 95.8

Columns (1), (2), and (3) quoted from *Leiden Comm.*, **169c** (1924).
H. A. Kuypers and H. K. Onnes, *Leiden Comm.*, **165a** (1923) give for oxygen at 0 °C the equation $\frac{pv}{p_0v_0}$ 1.00095 − 95.803 × $10^{-5}\frac{v_0}{v}$ + 2.0608 × $10^{-6}\left(\frac{v_0}{v}\right)^2$ expressed in the symbols used here.

Measurements on oxygen obtained at the Leiden laboratory are quoted in Table 2. The values of α_1 in column 4 are insufficient to give an adequate determination of the variation of α_1 with density, which has been assumed in column 5 from Equation (6.3). The mean value of α_1 at one atmosphere (column 6) is in good agreement with the value obtained from the Reichsanstalt measurements, Equation (6.3).

7. Argon

The Reichsanstalt measurements on argon are quoted in Table 3 and values of α_1 are plotted in Fig. 1. It is apparent from line 4 that α_1 for argon is very

Table 3. Data on Argon at 0 °C and 1 to 100 Atmospheres Obtained by Holborn and Schultze.

p (m Hg) (1)	$\frac{pv}{p_0v_0}$ (2)	$10^5\left(1-\frac{pv}{p_0v_0}\right)$	$0.235\left(\frac{v_0}{v}-1\right)$	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$
19.230	0.97826	87.43	5.84	93.27
19.258	.97821	87.50	5.85	93.35
37.552	.95817	82.72	11.93	94.65
37.940	.95809	82.01	12.03	94.04
55.521	.94192	76.00	17.96	93.96
55.611	.94173	75.97	18.02	93.99
74.395	.92746	69.39	24.57	94.01
74.408	.92746	69.38	24.58	93.95
				Mean = 93.90

Columns (1) and (2) quoted from *Ann. der physik*, **47**, 1089 (1915). The details of the measurements, such as quoted for oxygen, are not given. It is assumed here that the reference pressures, p_0, were sufficiently close to 760 mm Hg that corrections would amount to less than 1 in $10^5\alpha_1$. See notes on the measurements of Holborn and Schultze on helium for evidence in support of this assumption.

similar to α_1 for oxygen (line 3). The equation for line 4, obtained graphically,* is

$$\frac{pv}{p_0v_0} = 1 - 93.90 \times 10^{-5}\left(\frac{v_0}{v} - 1\right) + 0.235 \times 10^{-5}\left(\frac{v_0}{v} - 1\right)^2 \qquad (7.1)$$

which yields $10^5\,\alpha = -93.9$ at 0 °C and one atmosphere. The equation given by Holborn and Otto[4] based on the same data, yields $10^5\,\alpha = -98.1$ at one atmosphere. The difference, about 4 per cent, is about the same as that previously found for oxygen, and for the same reason.

Measurements obtained on argon at the Leiden laboratory are quoted in the first part of Table 4. The values of $10^5\,\alpha_1$, ranging from −72 to −75, were not plotted in Fig. 1 because they are grossly inconsistent with the Reichsanstalt data as pointed out by Holborn and Schultze. A plausible clue to the reason for the large discrepancy is given by Wild[1] in a footnote, quoted as follows: "Professor Masson of the University of Durham informs me that Onnes' data on argon are in error, due to "side trapping" of a small amount of gas in one limb of the piezometer, after measurement of its volume at one atmosphere."

Table 4. Data on Argon at 0 °C and 1 to 62 Atmospheres Obtained by Onnes and Crommelin.

$\frac{p}{p_0}$ (1)	$\frac{v_0}{v}$ (2)	$\frac{pv}{p_0v_0}$ (3)	$\dfrac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$ (4)	$0.235\left(\frac{v_0}{v}-1\right)$ (5)	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$ (6)
20.576	20.877	0.98560	72.4	—	—
26.070	26.581	.98077	75.2	—	—
31.572	32.302	.97740	72.2	—	—
36.743	37.782	.97250	74.8	—	—
49.871	51.840	.96201	74.7	—	—
62.230	65.325	.95261	73.7	—	—
(Reference volume, v_0, increased by the factor 1.0035)					
20.576	20.950	0.98215	89.5	4.7	94.2
26.070	26.674	.97736	88.2	6.0	94.2
31.572	32.415	.97399	82.8	7.4	90.2
36.743	37.914	.96911	83.7	8.7	92.4
49.871	52.021	.95867	81.0	12.0	93.0
62.230	65.554	.94929	78.6	15.2	93.8
				Mean =	93.0

Columns (1), (2), and (3) quoted from *Leiden Comm.*, **118b** (1910).
Column (4). These values of α_1 are inadequate to establish the change of α_1 with density.
Column (5). The value 0.235 was assumed from the Reichsanstalt data on argon, Equation (7.1), since the data in column 4 are insufficient to yield an adequate value for the change of α_1 with density.

By choosing one of the high-pressure measurements as the reference state and eliminating v_0 at one atmosphere, it may readily be shown that the data at one atmosphere are not consistent with the data at the higher pressures. The value of v_0 obtained by this process is greater by the factor 1.0035. The calculations made on this basis in the second part of Table 4 lead to a value of $10^5\,\alpha = -93$

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* Least squares methods were not used in this case, because the corrections to $p_0=760$ could not be applied, the details of the measurements not being given by Holborn and Schultze. The results (see Fig. 1) parallel those for oxygen so closely that $10^5\,\alpha = -94 \pm 1$ at one atmosphere was taken as a reasonable estimate from a large-scale plot.

at one atmosphere, which is in fair agreement with that obtained from the Reichsanstalt measurements.

Attention is called to the fact that Onnes and Crommelin reported data for argon on 16 different isotherms which are quoted in "International Critical Tables," Vol. III, p. 4. All the data are based upon what appears to be an erroneous value for v_0.

8. Hydrogen

In the measurements at the Reichsanstalt and also the Leiden laboratory, large corrections are required since large portions of the gas were at about room temperature instead of the particular isotherm under investigation. In the measurements at the van der Waals laboratory of the University of Amsterdam by Michels and collaborators, there are no such corrections, since all the gas was at the same temperature, confined over mercury in a glass piezometer shaped somewhat like a McLeod gauge, with a large lower bulb for determinations of v_0 at one atmosphere and a series of small upper bulbs with electric contacts sealed into the capillaries between the small bulbs. With the same pressure inside and outside the glass piezometer, the measurements were carried to much higher pressures. The precision of the measurements is much higher than in any other measurements available. The measurements obtained on hydrogen are quoted in Table 5. With only six measurements of pv/p_0v_0, these were represented by a power series with five coefficients, only the first 3 coefficients being given in the publication cited, which yield $10^5\,\alpha = 61.16$ at 0 °C and one atmosphere. The reliability of this value is difficult to estimate under the circumstances.

Considerable effort has been devoted here to finding simple, yet adequate, interpolation equations in order that the advantages of least squares methods may be fully utilized without undue labor, and as an aid in obtaining impersonal estimates of uncertainties in α at low pressures. Many people, including the author, rebel at using least squares methods when more than about two unknown coefficients are involved, and especially when the number of observations approaches the number of unknown coefficients.

Table 5. Data on Hydrogen at 0 °C and 1 to 700 Atmospheres Obtained by Michels, Nijhoff, and Gerber.

$\frac{p}{p_0}$ (1)	$\frac{v_0}{v}$ (2)	$\frac{pv}{p_0v_0}$ (3)	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$ $10^5\alpha_1$	$\frac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}$ $10^5\alpha_2$	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{p}{p_0}-1}$ $10^5\alpha_3$	$\frac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{p}{p_0}-1}$ $10^5\alpha_4$
75.795	72.334	1.04785	67.08	65.51	63.97	62.48
164.193	148.221	1.10776	73.196	69.515	66.032	62.711
268.99	227.641	1.18164	80.144	73.642	67.779	62.278
442.27	338.39	1.30698	90.987	79.350	69.569	60.670
556.89	400.47	1.39059	97.777	82.541	70.264	59.315
701.34	468.89	1.49575	105.954	86.052	70.787	57.490

In Fig. 2 the coördinates of the points on the four curves are as follows:

3 & 4	1 & 2		1	2	3	4

Columns (1) and (2) quoted from *Ann. der physik*, 12, 562 (1932). Values in other columns were computed from these experimental values.

As an illustration of the characteristics of the four different α's defined by Equations (4.1) to (4.4), calculated values over a wide interval are given in Table 5 and are plotted as open circles in Fig. 2, the numbers 1 to 4 on the curves corresponding to α_1, α_2, α_3 and α_4 respectively. For curves 1 and 2, the abscissae are v_0/v, and for curves 3 and 4, the abscissae are $\frac{p}{p_0}$. Obviously, curves 1, 3, and 5 cannot be represented adequately by a linear equation; even a quadratic equation is insufficient. Curve 2 is apparently linear within the precision of the data and the equal weight, least squares equation is

$$10^6 \ln \frac{pv}{p_0v_0} = (61.869 \pm 0.073)\left(\frac{v_0}{v} - 1\right) + 0.05175\left(\frac{v_0}{v} - 1\right)^2 \qquad (8.1)$$

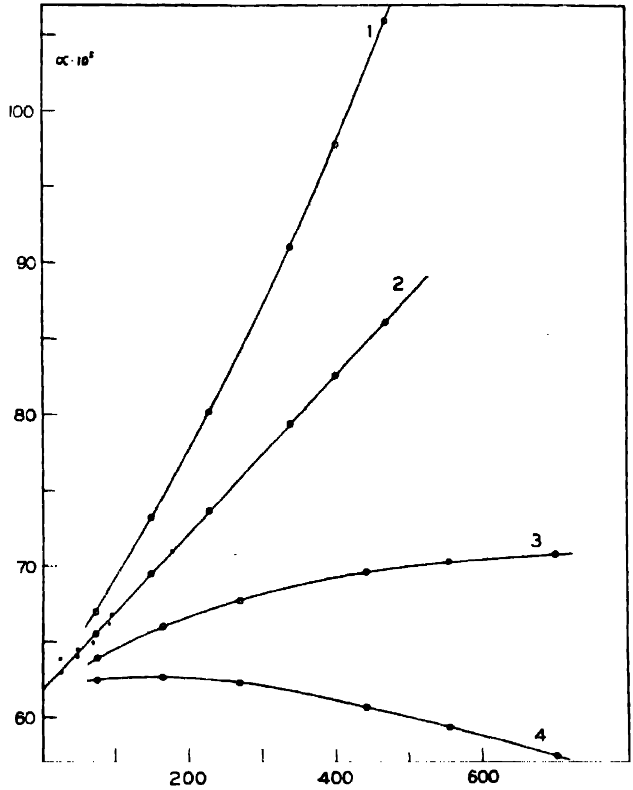

FIG. 2. Data on hydrogen at 0 °C. Curves 1, 2, 3, and 4 represent α_1, α_2, α_3, and α_4 respectively calculated in Table 5 from data of Michels, Nijhoff and Gerber (open circles). The abscissae for curves 1 and 2 are v_0/v; for curves 3 and 4 the abscissae are p/p_0. Data of Holborn are represented by crosses; data of Wiebe and Gaddy are represented by inked circles.

On a large-scale drawing, using a straight-edge for curve 2 and a celluloid spline, held in place by lead weights for drawing curves 1, 3, and 4, it was apparent that all four curves tended to approach smoothly the same value of α at one atmosphere to about three significant figures.

The measurements of other observers on hydrogen are not given in detail here in order to conserve space. For purposes of comparison, values for α_2 from two other laboratories are also shown in Fig. 2. Mean values at about 25, 50, 75 and

100 atmospheres obtained from 11 measurements reported by Holborn,[5] when corrected as previously indicated for oxygen and when the slope of line 2, Fig. 2, is assumed to be that given by the last coefficient in Equation (8.1), lead to an equal weight, mean value of $10^5 \alpha = 61.6 \pm 0.3$ at one atmosphere, while the equation given by Holborn gives $10^5 \alpha = 62.4$. The four measurements reported by Wiebe and Gaddy[6] at 25, 50, 100, and 200 atmospheres, yield an equal weight, mean value of $10^5 \alpha = 62.0 \pm 0.3$ at one atmosphere, when the slope of line 2, Fig. 2, is assumed as stated above.

The agreement of three values at one atmosphere for $10^5 \alpha$, namely, 61.87 ± 0.07, 61.6 ± 0.3, and 62.0 ± 0.3, obtained from measurements in three different laboratories is very gratifying and very significant, if it is interpreted as evidence that systematic errors in measurements made in these laboratories were small. The foregoing values are consistent with the extensive measurements on hydrogen at 20 °C, made at the Leiden laboratory with a multiple-column, open-end, mercury manometer by Schalkwijk,[7] when α_2 is calculated and compared with the measurements indicated by line 2, Fig. 2. The measurements reported by Nijhoff and Keesom[8] at 0 °C, made with a closed-end mercury manometer, are less precise and lead to a value for α at one atmosphere which is lower than those given above by a few per cent.

9. Nitrogen

Measurements on nitrogen obtained at the van der Waals laboratory of the University of Amsterdam are quoted in Table 6. Michels, Wouters, and de Boer state that "series evaluation . . . . carried out according to the method of mean squares" yielded the following equations:

Table 6. Data on Nitrogen at 0 °C and 1 to 52 Atmospheres
Obtained by Michels, Wouters, and de Boer.

			10^5 (observed-calculated)			
$\frac{p}{p_0}$ (1)	$\frac{v_0}{v}$ (2)	$\frac{pv}{p_0v_0}$ (3)	Equation (9.1) (4)	Equation (9.2) (5)	Equation (9.3) (6)	Equation (9.4) (7)
19.0215	19.1606	0.99274	−4	−5	−4	−4
23.7629	23.9734	.99122	1	1	1	2
28.4968	28.7894	.98983	6	6	6	7
33.1101	33.4951	.98851	1	1	1	2
37.9526	38.4409	.98730	−1	−1	0	0
42.7435	43.3413	.98621	−6	−6	−5	−5
47.4376	48.1401	.98541	4	3	3	3
52.2160	53.0328	.98460	0	0	−3	−3

Columns (1), (2), (3), (4), and (5) quoted from *Physica* (7), I, 587 (1934).

$$10^5 \frac{pv}{p_0v_0} = 100045 - 46.020 \frac{p}{p_0} + 0.30048\left(\frac{p}{p_0}\right)^2 - 1.35 \times 10^{-7}\left(\frac{p}{p_0}\right)^4 \qquad (9.1)$$

$$10^5 \frac{pv}{p_0v_0} = 100045 - 45.860 \frac{v_0}{v} + 0.30643\left(\frac{v_0}{v}\right)^2 - 1.84 \times 10^{-8}\left(\frac{v_0}{v}\right)^4 \qquad (9.2)$$

which were obtained from their paper but are expressed in the symbols used here.

In order to test the effect on α at one atmosphere when a different form of equation was used and also to obtain an estimate of uncertainty, the following least squares equation

$$10^5 \ln \frac{pv}{p_0v_0} = (-45.3166 \pm 0.308)\left(\frac{v_0}{v} - 1\right) + 0.29868\left(\frac{v_0}{v} - 1\right)^2 \qquad (9.3)$$

was obtained from the same data, weighting each observation proportional to $\left(\frac{v_0}{v}-1\right)$. As a check, the calculations were repeated giving each observation equal weight, which yielded

$$10^5 \ln \frac{pv}{p_0v_0} = (-45.3236 \pm 0.352)\left(\frac{v_0}{v}-1\right) + 0.29885\left(\frac{v_0}{v}-1\right)^2 \tag{9.4}$$

A comparison of the four equations is given in Table 6, where the deviations of Equations (9.1) and (9.2) have been copied from Table 2 of the paper by Michels, Wouters, and de Boer. There is obviously very little difference between the various equations as far as representing the measurements is concerned, but there is considerable difference in the labor required to obtain 4 unknown coefficients in Equations (9.1) and (9.2) and only 2 coefficients in (9.3) and (9.4) which were calculated with the equation in the linear form

$$x_2 = A + Bx \quad \text{or} \quad \frac{\ln \frac{pv}{p_0v_0}}{\frac{v_0}{v}-1} = A + B\left(\frac{v_0}{v}-1\right) \tag{9.5}$$

Furthermore, calculation of the uncertainty in α at one atmosphere from equations such as (9.1) and (9.2) is complicated, while such a calculation is simple with Equation (9.5). Differentiation of each equation gives for α at one atmosphere

$-10^5\alpha$	Equation
45.42	(9.1)
45.25	(9.2)
45.32 ± 0.31*	(9.3)
45.32 ± 0.35*	(9.4)

Michels, Wouters, and de Boer give some discussion of uncertainties in their measurements. The total volume, v_0, of the piezometer is given as about 1500 cm³, which means that the actual volumes of the gas at 0 °C and 19 to 52 atmospheres were between about 75 to 30 cm³.

In a joint publication from the Reichsanstalt and the University of Amsterdam, Otto, Michels, and Wouters[9] report measurements on nitrogen at 0 °C and 45 to 227 atmospheres, in which the volume, v_0, of the piezometer is stated to be about 98 cm³ and the volumes at high pressure to be between 2 and 0.43 cm³. With 9 different measurements of pv/p_0v_0, these authors represent their results at 0 °C by means of two equations similar in form to Equations (9.1) and (9.2) but with two more coefficients for sixth and eighth power terms, making a total of 6 coefficients. The authors do not state that the method of least squares was used in obtaining their equations, which upon differentiation yield two values for $-10^5\alpha$ at one atmosphere, namely, 45.31 and 44.70, corresponding to equations similar to (9.1) and (9.2) respectively.

Uncertainties in these two values are difficult to estimate under the circumstances, but it seems safe to infer from the evidence available that the true uncertainty in any value of α at one atmosphere, obtained from the same measurements by any accurate method of calculation, would exceed the true uncertainty in the value of α obtained from the measurements quoted in Table 6. In other words, the values of α at one atmosphere obtained from the two investigations may be said to be in agreement, or at least not in conflict, within reasonable estimates of uncertainties. Apparently the same statement might be applied to the values of α for nitrogen at 0 °C and one atmosphere obtained from many other investigations, some of which are listed by Otto, Michels, and Wouters,[9] while Keesom and Tuyn[10]* list from 15 different sources values of $-10^5\,\alpha$ which range from 37.2 (credited to Amagat) to 54.1 (credited to Bartlett).

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* See Equation (5.2) for the interpretation of $\pm u$ as used here. Readers accustomed to thinking in terms of least squares probable error should mentally divide $\pm u$ by 3.

No attempt can be made here to give an adequate discussion of calculations of the slopes of isotherms other than 0 °C, but it may be of interest to outline briefly a possible procedure in examining the reliability of data available on nitrogen at 100 °C. Suppose an equation similar to (9.4) but written in the more general form

$$\ln \frac{pv}{p_0v_0} = A + B\frac{v_0}{v} + C\left(\frac{v_0}{v}\right)^2 + \dots \tag{9.6}$$

is assumed for the 100 °C isotherm, and that the coefficients A, B, and C are determined by least squares methods, using the data given by Michels, Wouters, and de Boer, which include 8 values† of pv/p_0v_0 at 100 °C for the same values of $\dfrac{v_0}{v}$ quoted in Table 6. Subtracting two such equations, one for 100 °C and one for 0 °C, already obtained, yields

$$\ln \frac{(pv)_{100^\circ}}{(pv)_{0^\circ}} = (A_{100} - A_0) + (B_{100} - B_0)\frac{v_0}{v} + (C_{100} - C_0)\left(\frac{v_0}{v}\right)^2 + \dots \tag{9.7}$$

It so happens that for nitrogen, C_{100} is very nearly equal to C_0, so that at constant volume $\ln \dfrac{p_{100^\circ}}{p_{0^\circ}}$ is very nearly linear in v_0/v over the range covered. Visual evidence of this is given in Fig. 3, where a linear scale of logarithms is used for the ordinates. The three points near the ordinate axis were obtained from the constant-volume, gas-thermometer measurements of Beattie.[11] While measurements are reported at five different pressures, two intermediate points are not shown, for clarity. The other 8 points were obtained from the essentially constant-volume gas-thermometer measurements of Michels, Wouters, and de Boer, and the line was drawn with a straight-edge. The data from the two investigations appear to be mutually consistent to a few parts in 10^5, and consistent with an intersection with the ordinate axis between 1.3660 and 1.3661 on a large-scale plot.

It may be noted that

$$\ln \frac{(pv)_{100^\circ}}{(pv)_{0^\circ}} \doteq \ln \frac{T_{100}}{T_0} \doteq A_{100} - A_0 \quad \text{as} \quad \frac{v_0}{v} \doteq 0$$

and

$$T_0 \doteq \frac{100}{\dfrac{T_{100}}{T_0} - 1},$$

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* This reference may be consulted for an extensive bibliography of p,v,T data on He, H_2, and N_2.

† In obtaining the values of pv/p_0v_0 at 100 °C, corrections were applied by Michels, Wouters, and de Boer for changes in volume of the glass piezometer with temperature and pressure, and for the fact that the temperature actually observed was 99.720 °C instead of 100 °C. No mention is made of a correction for the vapor pressure of mercury, which is known to be about 0.0004 atmosphere at 100 °C. The effect of such a correction, if not already applied, would be to lower slightly the points shown in Fig. 3, a perceptible amount at $v_0/v = 19$ on a large-scale plot, and barely perceptible at $v_0/v = 52$.

by definition; hence

$$T_0 = \frac{100}{e^{(A_{100}-A_0)} - 1}.$$

Thus, a value for T_0, the ice point on the thermodynamic scale, may be obtained from the measurements of Michels, Wouters, and de Boer, but the calculated uncertainty in T_0 would obviously turn out to be relatively large.

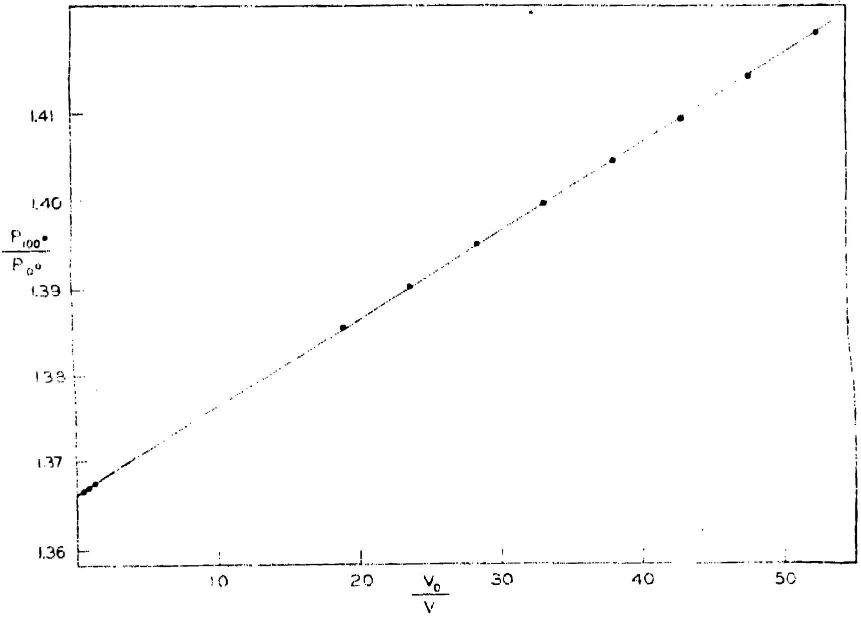

FIG. 3. Data on the ratio of pressures at 100 and 0 °C obtained with nitrogen at constant volume by Beattie below two atmospheres and by Michels, Wouters and de Boer at 19 to 52 atmospheres.

A value of T_0 has been calculated by Beattie[11] based entirely on his measurements with nitrogen. He has also calculated values of T_0 using in principle three different values for the rate of change of $p_{100^\circ}/p_{0^\circ}$ obtained by various round-about processes from measurements of Joule-Thomson coefficients, or of pv/p_0v_0 at higher pressures which make the calculation of uncertainties very complicated. A more direct method of calculation of T_0 from the data on nitrogen appears to be to combine the two sets of data shown in Fig. 3, using the observed ratios $p_{100^\circ}/p_{0^\circ}$. This may be done in several different ways.

One method is to use an adequate form of equation, preferably with a minimum of unknown coefficients, and a judicious assignment of weights to each observation. This method gives the high-pressure data the weight to which they appear entitled. Another method, which seems to lead to essentially the same final result and is sometimes preferable because it is simpler, is to combine the data at low and high pressures to obtain a value for the rate of change of $p_{100^\circ}/p_{0^\circ}$ with either p/p_0 or v_0/v and to use this value to reduce each individual observed ratio $p_{100^\circ}/p_{0^\circ}$ near the ordinate axis and thus obtain a weighted mean value for $p_{100^\circ}/p_{0^\circ} = T_{100}/T_0$.

In spite of the apparent advantages of these two methods of calculation, neither of them has ever been used to calculate T_0 or the uncertainty in T_0.

In this connection, it may be noted that the rate of change of $p_{100^\circ}/p_{0^\circ}$ at low pressures may be calculated from the measurements of Beattie alone, or it may be calculated using only the measurements of Michels, Wouter, and de Boer and a method similar to the one outlined above. When consideration is given to the possible effects of constant or systematic errors in each investigation, it seems probable that a combination of both sets of data should yield a more reliable value for the rate of change of $p_{100^\circ}/p_{0^\circ}$, which is larger and hence of more importance for nitrogen than for some of the other thermometric gases. The result of such a combination leads to a relative value for the slopes at low pressures of the pv isotherms at 0 and 100 °C, or for practical purposes a value for $B_{100} - B_0$ in Equation (9.7) or similar equations, and the uncertainty in the value for this difference may be calculated. It is emphasized that this procedure seems preferable to the one usually followed, namely, to obtain values for B_{100} and B_0 from the data on each isotherm separately, and then to obtain the difference. A value for $B_{100} - B_0$ may be calculated from measurements of the Joule-Thomson coefficient and the specific heat at constant pressure, but calculations of uncertainties are very complex, in fact impossible, since most of the primary Joule-Thomson data are reported in graphical form only. Apparently there are no Joule-Thomson measurements below one atmosphere pressure. Short extrapolations of pv data at constant volume or constant pressure appear to introduce no greater uncertainties in calculations of T_0 than the necessary extrapolations of Joule-Thomson data in order to apply them to gas-thermometer data at pressures below one atmosphere.

Another method of calculation, namely, a method of successive approximations, which may be used to advantage in the special case * when the data are given at constant volume or density, is to use Equation (9.6) or (9.7) or an equivalent equation in the form

$$\ln \frac{(pv)_t}{(pv)_{0^\circ}} = \ln \frac{T}{T_0} + (B_t - B_0)\frac{v_0}{v} + (C_t - C_0)\left(\frac{v_0}{v}\right)^2 + \dots \qquad (9.8)$$

where $v_t = v_{0^\circ}$ and v_0 is the reference volume at 0 °C and one atmosphere. A value

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* In the more general case, when the values of pv/p_0v_0 at 0 °C and on the isotherm, T, are not given at constant volume or density and gas-thermometer data at low pressures are lacking, the following procedure may be used for a first approximation. In addition to assuming a value for T/T_0, a value at 0 °C and $v_0/v = 0$ may be assumed for $pv/p_0v_0 = RT_0/p_0v_0$, designated by $1 + \lambda$ in "International Critical Tables," Vol. III. Each individual value for pv/p_0v_0 on any isotherm, T, may then be converted to

$$\frac{pv}{p_0v_0} \cdot \frac{p_0v_0}{RT_0} \cdot \frac{T_0}{T} = \frac{pv}{RT}.$$

Equation (9.6) may then be written in the form

$$\ln \frac{pv}{RT} = B\frac{v_0}{v} + C\left(\frac{v_0}{v}\right)^2 + \dots$$

or better still in the form

$$\alpha_0 = \frac{v}{v_0} \ln \frac{pv}{RT} = B + C\frac{v_0}{v} + \dots .$$

Thus values for α_0 may be plotted against v_0/v and approximate values for B and C may be obtained easily. A method similar to this has been applied to data on CO_2 over a wide range of pressures and in the critical region by the Demings, *Phys. Rev.* **56,** 108 (1939).

for T_0 may be assumed and any error in t °C, observed or reported, may be neglected for the first approximation, yielding a value for $T/T_0 = 1 + t/T_0$. Values for $(B_t - B_0)$ and $(C_t - C_0)$ may be obtained from data on $p_t/p_{0°}$ at the higher pressures by graphical or least squares methods, and these values used to correct low-pressure, constant-volume gas-thermometer measurements to obtain a better value for T/T_0; and the process may be repeated, if necessary. The calculations may be made conveniently with Equation (9.8) in the form

$$y = \frac{v}{v_0} \ln \frac{p_t}{p_{0°}} \frac{T_0}{T} = (B_t - B_0) + (C_t - C_0)\frac{v_0}{v} + \ldots \tag{9.9}$$

since calculated values of y usually do not vary much over a moderate range of v_0/v. Values of y may be plotted on a sufficiently open scale to determine how many terms to use or to inspect the data for evidence of anomalous trends. Such trends may be caused by systematic errors in the assumed values for T_0 and t °C or elsewhere * in the measurements of pv/p_0v_0.

In applying this method of calculation to the particular case of the 8 pairs of values of pv/p_0v_0 given by Michels, Wouters, and de Boer, each pair of values are at constant volume, giving one value for $p_{100°}/p_{0°}$ used in plotting Fig. 3. It may be noted that assuming $T_0 = 273.16 \pm 0.02$ and neglecting any error in the reported values for $t = 0$ °C and $t = 100$ °C gives $T_{100}/T_0 = 1.36609 \pm 0.00003$ as a point on the ordinate axis of Fig. 3 which may be used in the calculations to replace, in effect, the low-density gas-thermometer measurements of Beattie or of other observers. The true uncertainty in this value is probably less than the true uncertainty in any of the values of $p_{100°}/p_{0°}$ at higher densities. If the curve or the equation for the curve is not restricted at low densities, such as in least squares calculations using Equation (9.7) and the 8 higher points above, small errors, especially in the lower one or two points, may be so magnified as to lead to an intersection with the ordinate axis at 1.3663, which is far outside the limits of uncertainty assumed above, and the value for the slope of the curve at low densities, essentially $B_{100} - B_0$, is likewise more uncertain than when the equation for the curve is restricted at $v_0/v = 0$.

A reliable value for the ratio T/T_0 is the goal sought in most measurements with a constant-volume gas thermometer. Several different tables of corrections to be applied to measurements made at different temperatures with nitrogen or other gases with different ice-point pressures have been published. Values for such corrections are obviously a great convenience in gas-thermometer calculations, but the reliability of some of the published values may be questioned, since many of the corrections depend upon values for $B_{100} - B_0$ and $B_t - B_0$ calculated from data on pv/p_0v_0 at high pressures on each isotherm separately, without restriction at low pressures in some instances, with $T_0 = 273.09$ or $T_0 = 273.20$ in other instances, and with many other uncertainties involved, some of which are mentioned in other sections of this paper.

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* The data at 0 and 100 °C given by Michels, Wouters, and de Boer, when treated as outlined in the next paragraph, show an anomalous trend which appears to be too large to be caused by the vapor pressure of mercury at 100 °C or by reasonable errors in the temperatures reported or in $T_0 = 273.16$. The value used for the coefficient of expansion of glass may be in error, or the cause may be a peculiar combination of errors in $p_{100°}$ and $p_{0°}$ at the lower densities, such as one measured after a compression and the other one measured after an expansion of the gas. Errors in the calibration of the piston gauge are evidently not involved, since the ratio $p_{100°}/p_{0°}$ reduces to a ratio of weights applied.

10. Helium

Measurements on helium at 0 °C and up to 1000 atmospheres obtained by Wiebe, Gaddy, and Heins are quoted in Table 7. These authors reported the following least squares equation:

$$\frac{pv}{p_0v_0} = 1.00059 + 52.17 \times 10^{-5}\frac{p}{p_0} - 3.876 \times 10^{-8}\left(\frac{p}{p_0}\right)^2 \qquad (10.1)$$

Table 7. Data on Helium at 0 °C and 1 to 1000 Atmospheres Obtained by Wiebe, Gaddy, and Heins.

$\frac{p}{p_0}$ *	$\frac{pv}{p_0v_0}$ *	$\frac{pv}{p_0v_0}$ (10.1)	calculated from equation (10.2)	(10.3)	$\Delta = (\text{obs.} - \text{calc.}) \cdot 10^5$ (10.1)	(10.2)	(10.3)
1	1.0000	1.00101	1.00000	1.00000	+101	0	0
100	1.0523	1.05237	1.05203	1.05205	−7	+27	+25
200	1.1036	1.10338	1.10363	1.10359	+22	−3	+1
400	1.2026	1.20347	1.20395	1.20352	−87	−135	−92
600	1.3003	1.29967	1.30043	1.29948	+63	−13	+82
800	1.3924	1.39315	1.39308	1.39307	−75	−68	−67
1000	1.4838	1.48353	1.48187	1.48336	+27	+193	+44
				$\left(\frac{\Sigma\Delta^2}{n-3}\right)^{\frac{1}{2}} =$	±85	——	
				$\left(\frac{\Sigma\Delta^2}{n-2}\right)^{\frac{1}{2}} =$		±123	±75

Quoted from *J. Am. Chem. Soc.*, **53**, 1721 (1931).

This equation is an illustration of many to be found in the literature that fail to represent the reference state of the gas, which should be taken as exact for purposes of calculation. It was mentioned previously, and is emphasized again, that the measurement of the volume, v_0, of the gas at 0 °C and one atmosphere takes the place of a measurement of the mass of the gas so that v_0/v is, in a sense, a density sometimes called Amagat density. Obviously Equation (10.1) and the observed values of pv/p_0v_0 quoted in Table 7 apply to a constant mass of gas at a constant temperature, but in the least squares solution to obtain Equation (10.1) the mass of gas was obviously not restricted to constancy.

As an illustration of the effect on the coefficients and the deviations when this restriction is imposed and the same general form of equation is assumed, the equation

$$\frac{pv}{p_0v_0} = 1 + (53.033 \pm 0.58) \times 10^{-5}\left(\frac{p}{p_0} - 1\right) - 4.802 \times 10^{-8}\left(\frac{p}{p_0} - 1\right)^2 \qquad (10.2)$$

was obtained from the same data by least squares, giving equal weight to each observation. It may be noted from Table 7 that the deviations from this equation are systematic, which suggests that another term is desirable. In fact, when the four different α's, Equations (4.1) to (4.4), are computed from the measurements quoted in Table 7 and plotted, a graph is obtained which is so similar to Fig. 2 in all respects, except for scale, that it is not reproduced here. For helium, as for hydrogen, α_2 appears to be linear in v_0/v over a wide range within the precision of the measurements. A least squares equation for α_2 written as

$$\ln\frac{pv}{p_0v_0} = (53.212 \pm 0.44) \times 10^{-5}\left(\frac{v_0}{v} - 1\right) + 8.000 \times 10^{-8}\left(\frac{v_0}{v} - 1\right)^2 \qquad (10.3)$$

was obtained from the same measurements, weighting each observation proportional to $\left(\frac{v_0}{v} - 1\right)$. It may be noted from Table 7 that Equation (10.3) is somewhat better than (10.1) or (10.2), according to the "Gauss" criterion sometimes used to express relative "closeness of fit" of different equations with a different number of coefficients. The random deviations from Equation (10.3) suggest that no improvement may be expected from the use of additional terms. A graph, similar to Fig. 2, suggests that more terms must be used to represent α_1, α_3, or α_4 adequately.

Measurements on helium at 0 °C and up to 100 atmospheres obtained at the Reichsanstalt are quoted in Table 8 and corrected, as previously explained in the section on oxygen. The data are insufficient to give an adequate value for the rate of change of α_3 with pressure, which has been assumed from Equation (10.2) in obtaining the values of α at one atmosphere shown in the last column. The mean values of $10^5\,\alpha$, 52.5 and 53.0, are in good agreement with the corresponding values, 53.0 and 53.2, obtained in Equations (10.2) and (10.3) from the measurements of Wiebe, Gaddy, and Heins.

Table 8. Data on Helium at 0 °C and 1 to 100 Atmospheres
Obtained at the Physikisch-Technische Reichsanstalt.

p mm Hg		p_0 mm Hg	v_0 ml	Observed $\frac{pv}{p_0v_0}$	Correction to $p_0=760$	Corrected $\frac{pv}{p_0v_0}$	$10^5\left(\frac{pv}{p_0v_0}-1\right)$	$10^5\,\alpha$* at $p=p_0$
Holborn and Schultze†, *Ann. der Physik*, **47**, 1089 (1915).								
19229	110.797	779.54	2698.51	1.01279	1	1.01280	52.7	52.8
19276	110.796	781.69	2697.70	1.01278	1	1.01279	52.5	52.6
37794	110.789	789.02	5175.17	1.02543	2	1.02545	52.2	52.4
38328	110.790	800.95	5168.76	1.02572	3	1.02575	52.1	52.3
							Mean = 52.5	
Holborn and Otto, *Z. Physik*, **10**, 367 (1922).								
55873	106.016	681.74	8367.9	1.03833	−5	1.03828	52.8	53.1
56304	106.016	685.91	8379.2	1.03858	−5	1.03853	52.7	53.0
72991	106.007	675.66	10907.8	1.04988	−6	1.04982	52.4	52.9
74497	106.007	689.95	10888.7	1.05123	−5	1.05118	52.7	53.2
							Mean = 53.0	

* Obtained from the data in the previous column and an estimated rate of change of α with pressure, 4.8×10^{-8}, obtained from data of Wiebe, Gaddy, and Heins [see Equation (10.2)].

† The data on p and pv/p_0v_0 are quoted from *Ann. der Physik*, **47**, 1089 (1915); the data on v, p_0 and v_0 are quoted from *Z. Physik*, **10**, 367 (1922) for the same values of p and pv/p_0v_0, which appears to establish that these details were omitted in the paper by Holborn and Schultze.

Burnett[12] reported the results obtained in two concordant series of measurements with helium at 0 °C, using two essentially identical metal containers, each with double walls, so that the pressures within and without the inner containers could be equalized. One container was evacuated and the other was filled with specially purified helium to a pressure of about 120 atmospheres. Opening an inter-communicating valve permitted equalization of pressure in the two inner containers. The valve was closed, one container was evacuated, and the process was repeated until the pressure was reduced to about one atmosphere after a series of six expansions. The unique feature claimed for the method is that the volumes of the two containers need not be measured and the two containers need not be exactly equal in volume. The calculations of the results, which appear to be straightforward, are too complex to reproduce here. Burnett gives an equation obtained by a "weighted least squares method" which appears to amount to the following, in the symbols used here

$$\frac{pv}{p_0v_0} = 1 + 52.430 \times 10^{-5}\frac{p}{p_0} \tag{10.4}$$

This result, obtained with a radically different experimental procedure, appears to be in reasonably good agreement with the measurements of the Reichsanstalt and of Wiebe, Gaddy, and Heins.

The more recent measurements on helium at 0 °C and up to 12 atmospheres obtained at the Leiden laboratory are quoted in Table 9. In spite of the special efforts to avoid errors, described in *Communications* 227a and 227b, it is evident that the results are seriously affected by systematic errors, and are not in as good accord with more precise measurements made in other laboratories as might be expected from the description and calculations given. Keesom and Van Santen represented the measurements quoted in Table 9 by a weighted least squares equation, which in the symbols used here, is

$$\frac{pv}{p_0v_0} = 1 + 50.28 \times 10^{-5}\left(\frac{v_0}{v} - 1\right) \tag{10.5}$$

Table 9. Data* on Helium at 0 °C and 1 to 12 Atmospheres Obtained by Keesom and Van Santen.

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\dfrac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$	Mean $10^5\alpha_1$
6.01487	6.00120	1.00228	45.6	46.0
6.02039	6.00632	1.00234	46.7	
6.05938	6.04541	1.00231	45.8	
6.75635	6.73732	1.00282	49.2	49.3
6.76536	6.74596	1.00288	50.1	
6.76787	6.74906	1.00279	48.5	
7.70675	7.67917	1.00359	53.8	52.7
7.71382	7.68803	1.00335	50.1	
7.69834	7.67063	1.00361	54.1	
8.94029	8.90267	1.00423	53.5	51.5
8.95584	8.92043	1.00397	50.1	
8.98098	8.94453	1.00405	51.0	
10.63712	10.58771	1.00467	48.7	50.3
10.64405	10.59301	1.00482	50.2	
10.65493	10.60214	1.00498	51.9	
11.48274	11.42075	1.00543	52.1	51.0
11.48867	11.42802	1.00531	50.9	
11.50026	11.44048	1.00523	50.1	
12.38806	12.32015	1.00551	48.7	49.1
12.43204	12.36263	1.00561	49.4	
12.45699	12.38790	1.00558	49.1	
12.46478	12.39543	1.00559	49.0	
				Mean = 50.0 ± 1.7

* Values in the first three columns are quoted from *Leiden Comm.*, **227b**, 1933, regrouped ording to values of $\frac{p}{p_0}$.

and the coefficient in this equation is stated to be accepted as "definitive" in connection with the present low-temperature scale used at the Leiden laboratory. As mentioned previously, pressures were measured with a closed-end manometer, apparently filled with hydrogen. The so-called "normal volume," represented by v_0 here, is stated to be 548.861 cm^3 at 0 °C, although actually measured "for practical reasons" at 18 °C and corrected to 0 °C. It is stated that a glass piezometer of 40 cm^3 capacity was immersed in an ice bath. A perusal of earlier communications, to which references are made, indicates that the 40 cm^3 piezometer when in the ice bath was probably connected by means of a flexible metal capillary to the top of a vertical glass tube (called the "stem of the piezometer" and stated to be 10.74 mm in diameter) maintained at 20 °C in a stirred water bath. With mercury between the "stem" and the closed-end manometer, the helium in the piezometer and "stem" and the hydrogen in the closed end of the manometer, were compressed to different pressures by means of auxiliary apparatus. At 6 atmospheres, more than half of the helium must have been at 20 °C instead of 0 °C. The exact manner of making the necessarily large correction does not appear to be given specifically in any of the communications examined, although similar measurements were made at 20 °C, apparently for use in making such corrections. Uncertainties in the volume of the gas beneath a plane tangent to the mercury meniscus in the (10.74-mm diameter) "stem" were recognized, and mention is made of x-ray shadowgraphs taken of this meniscus.

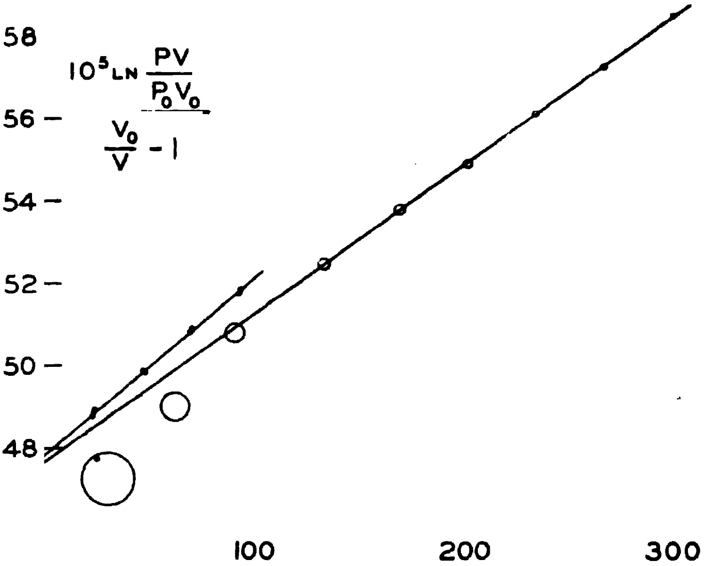

FIG. 4. Data on neon at 0 °C. Reichsanstalt data, small inked circles; data of Michels and Gibson, open circles with radii equivalent to uncertainty of 2 in 10^4 in pv/p_0v_0.

11. Neon

In Fig. 4 an illustration is given of an anomalous trend in α_2 obtained from measurements on neon reported by Michels and Gibson.[13] These measurements are among the earlier ones obtained in the van der Waals laboratory by the method outlined in the section on hydrogen. The authors state their estimate of accuracy to be about 2 in 10^4 and the radii of the open circles have been chosen to indicate this uncertainty.

The Reichsanstalt measurements[14] on neon, designated by small, black circles in Fig. 4, indicate the same normal trend in α_2 found for all the other gases considered. These measurements were corrected, as indicated previously in the section on oxygen. Glass containers were used in all of the Reichsanstalt measurements on gases previously discussed, with the same pressure inside and outside the glass, and small corrections were obviously applied for compression of the glass. In the measurements on neon, two different metal containers of the same diameter and wall thickness, but of different lengths, were used; and no corrections were made for the stretch of the containers with pressures up to 100 atmospheres inside and atmospheric pressure outside the containers. The metal containers were also used with nitrogen at temperatures up to 400 °C and measurements[15] were made at 0 °C and also 100 °C with the same pressure inside and outside the container, and also with atmospheric pressure outside. Apparently, the observed differences in volume were considered negligible for their purposes. The observed changes in volume are consistent with the value of 4.5×10^{-6} per atmosphere for $\frac{1}{v}\frac{dv}{dp}$, calculated from the dimensions given and the elastic properties of the metal.

Attention is called to the lack of concordance in the values of v calculated from the relation $v = v_0 \cdot [1 + at + bt^2]$ given for the volume of the metal container and the value of v actually used in the calculations[15] for the different gases at temperatures above 0 °C. The metal container, constructed by welding ends on a cylindrical tube, was apparently not annealed before the initial calibration was made by filling with toluene at 18 °C. After the container was used in measurements with several different gases at several different temperatures up to 400 °C, a subsequent calibration[14] with mercury disclosed that the container had shrunk more than 2 in 10^3. A change in volume of this order of magnitude would make a considerable change in all the α's at one atmosphere or the "B-values" calculated from the measurements at various temperatures with He, A, N_2, H_2, and a mixture of Ne and He. It seems probable that most of the shrinkage took place during the measurements at the higher temperatures with one of these gases, but the order of the measurements with the different gases is not definitely stated. There is a strong implication that measurements with nitrogen were made first, although the anomalous results, mentioned but not recorded, with hydrogen at 300 °C are in the right direction to be caused by such shrinkage; but this may also be explained satisfactorily on metallurgical grounds. The seriousness of this unfortunate situation is that these are the only available measurements on some of the gases at temperatures up to 400 °C, and it shakes the very foundations for several equations of state and many other conclusions based upon these measurements.

Uncertainties in the volume of the container at high temperatures in the measurements with neon[14] seem to be smaller than for the other gases, since rather convincing evidence is given that the container was adequately annealed by this time after numerous excursions to 400 °C. Fortunately, the order is given in which the experiments on any one gas were made, and a good check with neon at 0 °C is obtained before and after heating to 400 °C. No corresponding check is supplied for the other gases. Using values of pv/p_0v_0 for nitrogen at 0 °C up to 100 atmospheres, which were determined in glass containers and appear to be reliable to a few parts in 10^5, together with measurements on nitrogen at 0 °C obtained with metal containers, leads to values for the volumes of the metal containers which are about 2 in 10^4 larger than the values obtained in calibrations with mercury. This result appears to be in harmony with the results found by Kaminsky and Blaisdell,[16] who demonstrated that mercury does not fill the small crevices in metal surfaces which are filled by gases. When allowance is made for slightly greater volumes of the metal containers and also for their stretch, the value of α at 0 °C and one atmosphere obtained from the Reichsanstalt measurements on neon, indicated in Fig. 4, is about $49 \pm 1 \times 10^{-5}$.

A similar value with about the same uncertainty may be obtained from the measurements of Michels and Gibson by eliminating the reference state, p_0v_0, at 0 °C and one atmosphere and choosing one of the other states at higher pressures as a reference. When this is done, all the points indicated by the open circles in Fig. 4 are found to be represented by an equation of the form

$$\ln \frac{pv}{p_0v_0} = A + \frac{Bv_0}{v} + C\left(\frac{v_0}{v}\right)^2 \tag{11.1}$$

well within the author's estimated limits of 2 in 10^4 and leads to the value for α at one atmosphere stated above. The fact that the points shown in Fig. 4 cannot be represented within these limits by the same form of equation, when the one atmosphere reference state is used as a basis for the calculations, appears to be very strong evidence of a systematic error in the earlier calibration of the piston gauge or in the reference values, p_0, v_0, at 0 °C and one atmosphere. It may be noted that, when the reference state is changed to a state at high pressures and the one atmosphere data are excluded, all the ratios used in the calculations with Equation (11.1) are essentially ratios of weights applied to the piston gauge, while in the calculations of α_2 shown in Fig. 4, the effective area of the piston gauge is involved as previously indicated in Equation (5.8). The volume of the gas at 0 °C and one atmosphere was apparently not measured directly, but was calculated from a measurement at about 25 °C and one atmosphere and corrected to 0 °C in a manner described in several later papers from the same laboratory.

12. Reichsanstalt Measurements Below 2 Atmospheres

The latest measurements, obtained at the Reichsanstalt by Heuse and Otto[17] at 0 °C and at pressures below two atmospheres, yield the following values for $10^5\,\alpha$:

p_0* (mm Hg)	He	H_2	N_2
533.10	59	72	−25
727.17	38	46	−62
994.50	58	63	−55

$10^5\,\alpha$ from previous sections for comparison:

	He	H_2	N_2
	53.0	61.9	−45.3

These measurements were made after many years of experience in such measurements, and after improvements in apparatus and technique had been developed. It is the purpose of this section to investigate why these measurements yield such a wide scatter in α. There are reasons for expecting that the primary measurements of p and v at 0 °C with the apparatus and method employed should have been capable of yielding a precision of the order of a few units in 10^6, which is comparable to about one per cent in α, according to the analysis given in the section on uncertainties, when $\left(\frac{p}{p_0} - 1\right)$ is about 0.3, as it is in all these measurements. The scatter, however, is many times this amount and appears to be systematic with the different gases at certain values of p_0.

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* Throughout this section, p_0 is used to designate a reference state, sometimes called the ice-point pressure in a gas thermometer, in order to conform to common practice in gas thermometry. It should not be confused with the one atmosphere reference pressure used in other sections.

The measurements were made at the same time and are reported in the same publication containing the latest determinations of pressure and volume coefficients of expansion of these gases in a gas thermometer over the fundamental, 0° to 100 °C, interval which yield determinations of the thermodynamic temperature of the ice point, T_0. With each separate filling of the gas thermometer, measurements were made with a constant mass of gas in four different states, indicated in Fig. 5, where the point 0 is taken as the reference state for the group. Measurements at the states 1 and 0 yield a value for α or the slope of the 0 °C isotherm. Similarly, measurements at the states 2 and 3 yield a value for the slope of the 100 °C isotherm. Calculated values for the slope of the 100 °C isotherm, for thermometer fillings to different p_0's, expressed in terms of $\frac{10^6}{v_0}\left(\frac{dpv}{dp}\right)_t$ are:

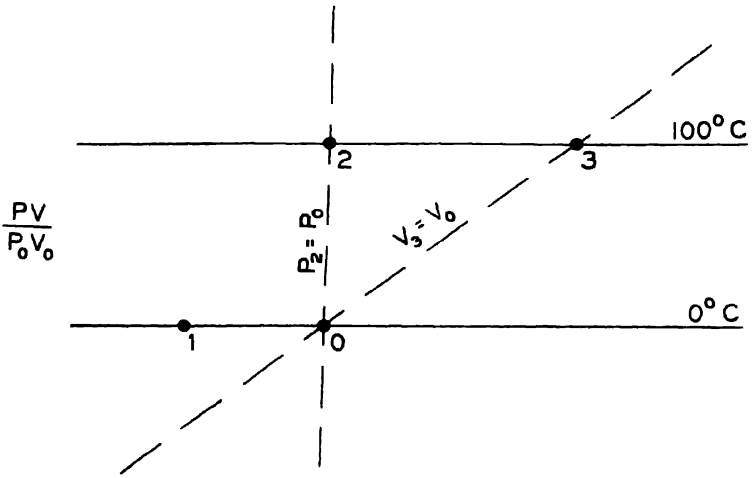

FIG. 5. Diagram of a group of Reichsanstalt measurements with one filling of their gas thermometer. Measurements at states 0 and 2 were made at constant pressure and states 0 and 3 were measured at constant volume.

p_0 (mm Hg)	He	H_2	N_2
390.24	74	69	48
533.10	31	35	12
727.17	68	77	28
994.50	52	66	12
Mean	56	62	25

Table 10. Calculations to T_0 from Reichsanstalt Measurements.

Date 1929	State (See Fig. 5)	t °C	p^* (m Hg)	v^* (cm³)	pv (m Hg-cm³)	$\frac{pv}{p_0v_0}$	$\frac{(pv)_{p=0}}{p_0v_0}$	$\frac{T_{100}}{T_0}$	T_0
Helium									
4/15		0	0.39024			1.000000	0.999727[a]	1.365961	273.253
4/15		100	0.53310			1.36611*	1.365588		
4/15		100	0.39024			1.36597*			
4/13		0	0.39024	425.624	166.0955	0.999889	0.999586	1.366286	273.011
4/13		0	0.53310	311.600	166.1140	1.000000			
4/13		100	0.72717			1.36602*	1.365720		
4/13		100	0.53310			1.36594*			
4/12		0	0.53310	428.199	228.2729	0.999903	0.999636	1.365714	273.438
4/12		0	0.72717	313.950	228.2950	1.000000			
4/12		100	0.99450			1.36611*	1.365217		
4/12		100	0.72717			1.36587*			
4/10		0	0.72717	426.301	309.9933	0.999797	0.999245	1.366146	273.115
4/11		0	0.99450	311.771	310.0563	1.000000			
4/11		100	1.36280			1.36604*	1.365115		
4/11		100	0.99450			1.36579*			
Hydrogen									
6/4	0	0	0.39024	——	——	1.000000	0.999680[a]	1.366122	273.133
6/4	3	100	0.53310	——	——	1.36617*	1.365685		
6/4	2	100	0.39024	——	——	1.36604*			
6/3	1	0	0.39024	425.383	166.0015	0.999865	0.999496	1.366482	272.865
6/3	0	0	0.53310	311.431	166.0239	1.000000			
6/3	3	100	0.72717	——	——	1.36613*	1.365793		
6/3	2	100	0.53310	——	——	1.36604*			
6/1	1	0	0.53310	426.572	227.4055	0.999881	0.999554	1.365805	273.370
6/1	0	0	0.72717	312.764	227.4326	1.000000			
6/1	3	100	0.99450	——	——	1.36620*	1.365196		
6/1	2	100	0.72717	——	——	1.36593*			
5/30	1	0	0.72717	426.938	310.4565	0.999777	0.999171	1.366159	273.105
5/30	0	0	0.99450	312.243	310.5257	1.000000			
5/31	3	100	1.36280	——	——	1.36621*	1.365026		
5/31	2	100	0.99450	——	——	1.36589*			
Nitrogen									
4/4	0	0	0.39024	——	——	1.000000	1.000234[a]	1.366074	273.169
4/4	3	100	0.53310	——	——	1.36673*	1.366394		
4/4	2	100	0.39024	——	——	1.36664*			
4/9	1	0	0.39024	427.567	166.8537	1.000047	1.000175	1.366356	272.959
4/9	0	0	0.53310	312.973	166.8459	1.000000			
4/9	3	100	0.72717	——	——	1.36671*	1.366595		
4/9	2	100	0.53310	——	——	1.36668*			
4/6	1	0	0.53310	427.205	227.7430	1.000159	1.000596	1.365904	273.296
4/5	0	0	0.72717	313.141	227.7067	1.000000			
4/5	3	100	0.99450	——	——	1.36709*	1.366718		
4/5	2	100	0.72717	——	——	1.36699*			
4/6	1	0	0.72717	428.357	311.4884	1.000192	1.000714	1.366203	273.073
4/8	0	0	0.99450	313.151	311.4287	1.000000			
4/8	3	100	1.36280	——	——	1.36740*	1.367178		
4/8	2	100	0.99450	——	——	1.36734*			

* Quoted values, all others are calculated values.

[a] Since measurements at state 1 were lacking, a value for the slope of the 0° isotherm was assumed in order to get at value for T_0 from this group.

The scatter is greater than for the 0 °C isotherm and departures from the mean appear to be systematic for all the gases at certain values of p_0

In the Reichsanstalt calculations of T_0, the two isotherms were assumed to be straight lines, but the values used for the slopes were obtained from pv measurements up to 100 atmospheres. The assumption of straight lines and the measurements at the four states, indicated in Fig. 5, are obviously sufficient to determine intersections of the two isotherms with the ordinate axis, which supply a value for

$$\frac{(pv)_{100}}{(pv)_0} = \frac{T_{100}}{T_0} \text{ and a value for } T_0 = \frac{100}{\frac{T_{100}}{T_0} - 1}$$

When T_0 is calculated from the measurements in this very direct manner, the results turn out as shown in Table 10 and also in Fig. 6, which again supplies unmistakable evidence of systematic departures from the mean value, represented by the horizontal line, for all the gases at certain values of p_0.

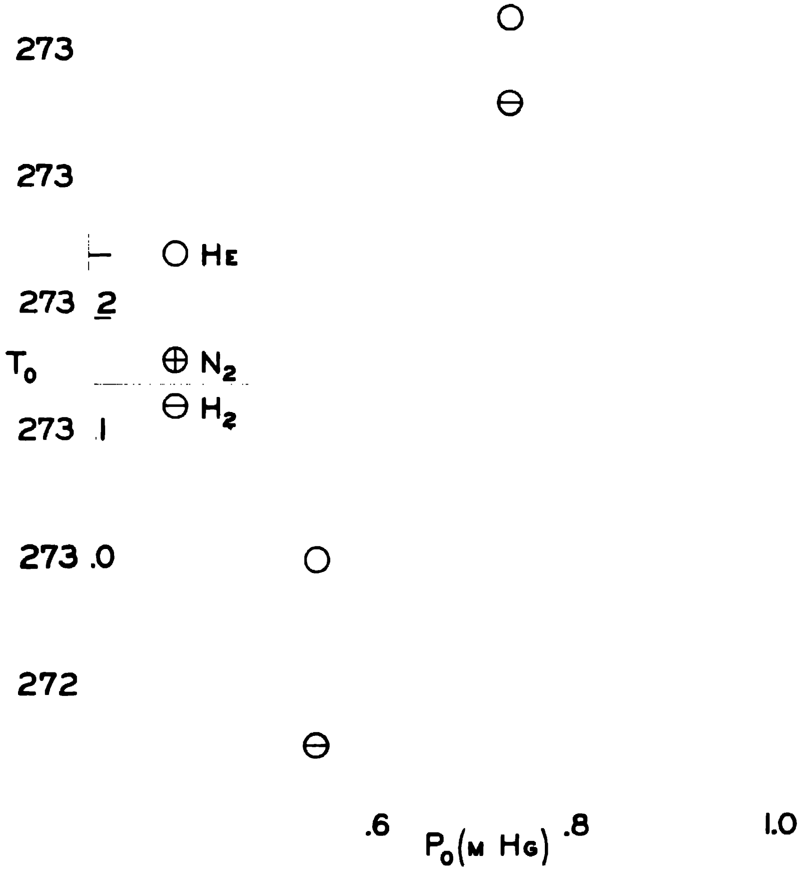

FIG. 6. Values for the temperature of the ice point, T_0, on the Thermodynamic Scale calculated from Reichsanstalt measurements on helium, hydrogen and nitrogen quoted in Table 10.

The scatter of the values for T_0 is much greater than the scatter of the published values for T_0, obtained from calculations using values for the slopes determined from high-pressure measurements. Errors in the slopes determined by the low-pressure measurements are evidently magnified in the calculated values for T_0, since the same values for states 0, 2, and 3 in Fig. 6 are used in both methods of calculation. One method gets a value for T_0 from points 0 and 2, and another value from points 0 and 3, with "accepted" slopes, while the method used above requires all four points to get one value for T_0.

Arguments might be advanced that the direct method of calculation used in Table 10 is the proper one to use, that the low-pressure measurements are sufficient in themselves, should stand on their own feet, and high pressure pv data should be ignored, as is done under similar circumstances when measurements of p and ρ are made for purposes of atomic weight determinations.[1] Magnification of errors, especially systematic errors in the slopes determined over a short interval, however, appears to make the other method of calculation, using slopes determined over a wide interval, the more reliable one to use. On the other hand, it may be argued that the measurements at state 1 are ignored and given no weight in the Reichsanstalt calculations of T_0, while equal weight is given to measurements at all four states in the calculations in Table 10.

A third method of calculation appears to have several advantages in this particular case, since it retains certain desirable features of each of the other methods and removes many of the systematic effects already mentioned by ignoring certain calibration measurements which are not described in detail, and uses instead measurements at state 1, thereby giving them considerable weight. In this method, the apparently more reliable values for the slopes supplied by high-pressure data are employed, as is done in the Reichsanstalt method, but are inserted into the calculations at an earlier stage in combination with measurements at states 1 and 0, Fig. 5. If such measurements yield an erroneous value for the slope at 0 °C, and if the errors are random or accidental, the chances are even that the measurements at state 0 may be in error and hence may lead to two erroneous values * for T_0 in the Reichsanstalt method of calculation, which in effect gives this point double weight, because it is used in calculating a constant-volume and also a constant-pressure coefficient of expansion, and with accepted slopes, two separate values for T_0. On the other hand, if the measurements at states 1 and 0 appear to be systematically in error, it is obviously desirable to make the calculations so as to eliminate the effect of the systematic errors.

The unique feature of the latest Reichsanstalt measurements, which is supposed to make them more reliable than similar earlier measurements leading to $T_0 = 273.20$, was the use of a specially constructed mercury manometer which was surrounded by ice. Several platinum wires were sealed into the glass walls at certain chosen heights and bent downward at the axis of a long vertical glass tube to serve as "prick points" at the center. Thus, all of the pressure measurements were made with definite fixed heights of mercury columns, as indicated in Table 10. The exact manner in which these heights were measured, once and for all, is not clearly described. It is mentioned, however, that the distances between prick points were measured at room temperature, although as used the manometer was at 0 °C. It is mentioned further that only pressure ratios are important and that the above circumstance should introduce no appreciable error in the ratios of heights, which would appear to be true if there were no vertical temperature gradients during the measurements at room temperatures, if the sealing-in processes at several points had no effect, and if the coefficient of linear expansion of the glass was the same throughout. No information is supplied relative to possible refraction errors in sighting through possibly non-uniform glass walls to the prick points or onto the mercury surface brought into "optical contact" with the prick points in the calibration of the manometer. All of these and other uncertainties in the calibration of the manometer, which appear to be the source of the systematic effects previously mentioned, may be eliminated as outlined below.

Although Heuse and Otto apparently did not realize it, they had at their dis-

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* A possible illustration of this is in the case of N_2 at $p_0 = 390$ mm (See Heuse and Otto's Table 7) where the reported values give for T_{100}/T_0, 1.36616 (constant pressure) and 1.36619 (constant volume), while the mean value for the 3 gases is 1.36609.

posal in reality, almost every day they took observations extending over a period of several months, an independent and reasonably reliable partial calibration of their manometer with each filling of their gas thermometer. Instead of inserting accepted values for slopes into the calculations near the end as they did, everything would have come out better if they had inserted the accepted slopes at 0 °C into the manometer calibration at the beginning. Instead of using the measured heights in the calibration of the manometer to calculate 0 °C slopes which scatter widely and were not used in the calculations later on, the same calculations may be reversed, since measurements at states 1 and 0, together with accepted slopes for the different gases, lead directly to several calibrations of the manometer. Although such calibrations yield only pressure ratios, these are the important quantities anyway.

Equation (4.3), together with the assumption of constant slope over the small interval covered by these measurements, gives

$$\alpha = \frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t = \frac{1}{v_0}\left(\frac{p_b v_b - p_a v_a}{p_b - p_a}\right)_t \tag{12.1}$$

where the subscripts refer to any two equilibrium states, a and b, of a given mass of gas at 0 °C, and v_0 is the volume of the same mass of gas at 0 °C and one atmosphere, which takes the place of a mass determination. All the values of α at one atmosphere, obtained in previous sections, are on this same basis and hence may be used to advantage in Equation (12.1) or any transformation of it. This is emphasized because the later calculations are made to serve a double purpose, one of which is to obtain a test of the reliability of the values of α for the different gases.

In order to get Equation (12.1) into a convenient form for the calculations at hand, the following steps are written out

$$p_b v_b - p_a v_a = \alpha v_0(p_b - p_a)$$

$$p_b(v_b - \alpha v_0) = p_a(v_a - \alpha v_0)$$

$$\frac{p_b}{p_a} = \frac{v_a - \alpha v_0}{v_b - \alpha v_0}$$

$$\frac{p_b}{p_a} = 1 + \frac{v_a - v_b}{v_b - \alpha v_0} \tag{12.2}$$

In the Reichsanstalt measurements, the quantity $(v_a - v_b)$ was directly measured by weighing displaced mercury, which is one of the simplest and most accurate of laboratory measurements. The quantity v_b was obtained from similar measurements of the volume of the gas thermometer bulb and the connecting glass tubing up to the lower mercury surface in the manometer. Using the measured volumes, quoted in Table 10, and values for v_0 to four figures easily obtainable from the column headed pv, and the values of α previously obtained, the following results are given in detail as an illustration.

Date	Gas	$10^6\alpha$	αv_0	v_b	$v_b - \alpha v_0$	$v_a - v_b$	$\frac{p_b}{p_a}$
4/12	He	53.0	0.1592	313.950	313.7908	114.249	1.364093
6/1	H_2	61.9	0.1852	312.764	312.5788	113.808	1.364094
4/5	N_2	−45.3	−0.1357	313.141	313.2767	114.064	1.364100
						Mean =	1.364096

These results supply the best direct experimental evidence available that the values for the slopes of the 0 °C isotherms below 2 atmospheres for these three gases are mutually consistent within reasonable uncertainties in these measurements. The maximum deviation from the mean ratio p_b/p_a is about 3 in 10^6, which appears to confirm the earlier statement that a precision of this order of magnitude should have been attainable in these measurements. To attain such a precision, of course, means that the two mercury surfaces in the manometer must be set in "optical contact" with the prick points with a precision of about 0.002 mm,* in the foregoing instances, since the recorded pressures, quoted in Table 10, are 533.10 and 727.17 mm Hg. But the ratio of these numbers, obtained from measurements of heights in the initial calibration of the manometer, is $p_b/p_a = 1.364041$. This value is different from the above mean by 40 in 10^6 which corresponds to a systematic error of about 30 per cent in all the α's, 0.017 cm^3 in $v_a - v_b$, (0.23g Hg) or 0.047 cm^3 in v_b (0.64g Hg), all of which appear to be unreasonably large. It seems more likely that the height measurements in the initial calibration are responsible for the difference.

When the same calculations are carried out using all the reported volume measurements, including oxygen ($10^5\,\alpha = -95.1$) and neon ($10^5\,\alpha = 49.0$), the results indicate a lower precision in several instances as shown below.

Calibration based on measurements of heights

p_b	533.10	727.17	994.50	1362.80
p_a	390.24	533.10	727.17	994.50
p_b/p_a	1.366082	1.364041	1.367631	1.370035

Calibrations based on isothermal slopes and measurements of volume, reported in Heuse and Otto's Table 2.

He	1.366067	1.364093	1.367608
H_2	1.366056	1.364094	1.367624
N_2	1.366031	1.364100	1.367675
O_2	1.366076	1.364081	1.367651
Ne†		———	1.367650†
Mean	1.366057	1.364092	1.367642

Calibration based on isothermal slope and measurements of volume, dated 2/6/1929 and reported in Heuse and Otto's Table 1.

He	1.366000	1.363969	1.367720	1.370275

There appears to be no convincing evidence in these results that the value used for α for any one gas is inconsistent with the values for the other gases. The scatter for the different gases at the third pressure ratio is about twice as large as at the other two ratios. One possible reason for this may be that a much longer piece of capillary tubing containing mercury at room temperature was used in the measurements of $v_a - v_b$ when the pressure exceeded atmospheric. Furthermore, it may be noted from Table 10 that the two states for He giving the lowest value (1.367608) were measured one day apart, and the two states for N_2 giving the highest value (1.367675) were measured two days apart, whereas the two states were measured on the same day for all the other gases at the corresponding ratio.

In the calibration calculated from the measurements, dated February 6, 1929, the conditions were different. These measurements were obtained before the gas thermometer bulb ($v = 297.134$ cm^3) was sealed onto the capillary tubing. All these measurements were made with one He filling ($v_0 = 70.38$ cm^3) and the mercury displacements were smaller (14.528 to 36.709 cm^3). Heuse and Otto do not give the diameter of the manometer tubing, but state that a change of 0.1 mm in the height of the mercury meniscus corresponds to a change of 0.005 cm^3 in the volume of the gas beneath a fixed plane tangent to the mercury-meniscus. All the differences from the means given above correspond to differences in the meniscus height in the two states of less than 0.2 mm, including the February 6, 1929 calibration. It seems likely that much of the scatter may be appropriately charged to differences in meniscus height rather than to corresponding errors up to 0.010 cm^3 (0.14 g Hg) in the volume measurements.

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* The author has had some experience which indicates that prick point settings on a mercury surface can be made to this precision without much difficulty.

† Calculated from volume measurements reported in *Ann. der Physik*, (4), **6**, 778 (1930).

When the mean values for the pressure ratios determined with several gases are used in later calculations, most of the systematic effects previously mentioned are removed, the scatter is markedly reduced, and there is general improvement all along the line. For example, the constant-volume coefficients for N_2 are brought into much better agreement with the measurements reported by Beattie.[11] While the constant-volume coefficients, β_v, are changed, the constant-pressure coefficients, β_p, are unchanged. The improvement in the differences, $\beta_p - \beta_v$, which are related to the 100 °C isotherm slopes, is illustrated below.

	–As reported (height calibration)–			–Gas Volume Calibration–	
p_0(mm Hg)	$10^7\beta_p$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$
		Helium			
390	36597	36611	14	36608	11
533	36594	36602		36607	13
727	36587	36611	24	36612	25
994	36579	36604	25	36604	25
		Hydrogen			
390	36604	36617	13	36614	10
533	36604	36613	9	36618	14
727	36593	36620	27	36621	28
994	36589	36621	32	36621	32
		Nitrogen			
390	36664	36673	9	36670	6
533	36668	36671	3	36676	8
727	36699	36709	10	36710	11
994	36734	36740	6	36740	6

Calculations of a mean value for T_0 and an uncertainty in T_0 from these Reichsanstalt measurements on the basis of a different manometer calibration have not been carried out for several reasons. It requires a recalculation of all of the foregoing values to one more place. Uncertainties in the values of the difference between the 0 and 100 °C isotherm slopes are involved, as are questions of weighting. It appears, however, that the major change is a smoothing of the data and a reduction in the calculated uncertainty without much change in the mean value for T_0. On the basis of these measurements, Heuse and Otto reported a mean value of $10^8 \beta = 366086$ which corresponds to $T_0 = 273.160$.

13. Measurements by Baxter and Starkweather

It is the purpose of this section: (1) to demonstrate that the measurements of Baxter and Starkweather obtained at 0 °C and one atmosphere or less are in substantial agreement, or at least do not seriously conflict, with the values of α already obtained from higher pressure measurements within the calculated uncertainties of the two sets of measurements; and (2) to illustrate that the calculated uncertainties in values for atomic weights and RT_0, based entirely on measurements at 0 °C and one atmosphere or less are larger than the calculated uncertainties based on both sets of measurements.

In the previous sections, the calculated uncertainties in α at one atmosphere were about one per cent or less. It was pointed out in Section 5 that one per cent in α was comparable to about 5 in 10^6 in pv/p_0v_0 for these gases over a range of ½ atmosphere. As shown in Table 11, the measurements of Baxter and Starkweather, which appear to be among the most precise measurements of this kind available, the calculated uncertainties in pv/p_0v_0 exceed the amount stated above and the calculated uncertainties in the α's range from 7 to 30 per cent. In every case, however, the values of α obtained from high-pressure measurements are well within the calculated limits of uncertainty in the low-pressure measurements as shown below.

Table 11. Measurements of the Density of Gases at 0 °C
Obtained by Baxter and Starkweather.

$\frac{p}{p_0}$	Pressure (mm Hg†)	Density (g/l) u	Uncertainty $10^6 u$	No. Obs.	$\frac{pv}{p_0v_0}$	$\frac{10^6\left(\frac{pv}{p_0v_0}-1\right)}{\frac{p}{p_0}-1}$ $10^6 \alpha_i$	Uncertainty $10^6 u$
		Oxygen [*Proc. Nat. Acad. Sci.*, **12**, 703 (1926)]					
1	760	1.428962 ± 10	7	6	1.000000 ± 00	—	—
3/4	570	1.071485 ± 29	27	20	1.000220 ± 28	−88.0	13
1/2	380	0.714154 ± 24	34	12	1.000458 ± 35	−91.6	8
1/4	190	0.356985 ± 17	48	10	1.000716 ± 48	−95.5	7
					Weighted* mean =	−93 ± 7	
		Nitrogen [*Ibid*, **12**, 703 (1926)]					
1	760	1.250361 ± 29	23	18	1.000000 00		
2/3	506.667	0.833482 ± 16	19	18	1.000110 ± 30	−33.0	27
1/3	253.333	0.416662 ± 16	38	14	1.000290 ± 44	−43.5	15
					Weighted* mean =	−41 ± 9	
		Neon [*Ibid.*, **14**, 57 (1928)]					
1	760	0.899902 ± 20	22	17	1.000000 ± 00		
2/3	506.667	0.600044 ± 30	50	11	0.999818 ± 55	54.6	30
1/3	253.333	0.300090 ± 26	87	12	0.999591 ± 90	61.5	22
					Weighted* mean =	59 ± 16	
		Argon [*Ibid.*, **14**, 57 (1928)]					
1	760	1.783640 ± 44	25	15	1.000000 ± 00		
2/3	506.667	1.188739 ± 45	38	7	1.000299 ± 45	−89.7	15
1/3	253.333	0.594193 ± 30	51	6	1.000594 ± 72	−89.1	12
					Weighted* mean =	−89 ± 12	

* Weighting each α_i inversely as the square of its uncertainty.
† At 0 °C and $g = 980.616$.

Gas	$10^6\,\alpha$ from measurements at high pressures	$10^6\,\alpha$ from measurements at low pressures	Differences in mean values (%)
O_2	−95.1 ± 0.9	−93 ± 7	− 2
N_2	−45.3 ± 0.3	−41 ± 9	−12
Ne	49 ± 1	59 ± 16	−20
A	−94 ± 1	−89 ± 12	− 5

The measurements of Baxter and Starkweather were apparently made by weighing all of these gases in glass "globes" of about 2-liter capacity, using the same manometer and technique throughout all these measurements. The constant sign of the differences between the mean values of α suggests the possibility of a systematic error in the measurements of density or pressure or both. According to the analysis given in Section 5, two per cent in α for O_2 corresponds to about 0.004 mm Hg in p, or about 0.02 mg in the weighings of 2-liter globes. That the difference is this small is high tribute to the care and skill of the observers.

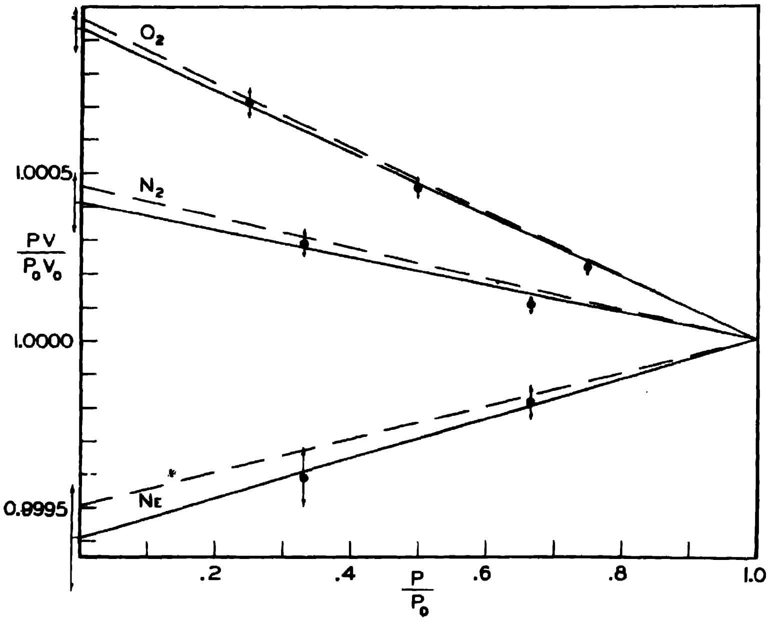

FIG. 7. Data at 0 °C by Baxter and Starkweather. Arrows indicate calculated uncertainties. Unbroken lines based on low-pressure measurements. Broken lines represent slopes calculated from high-pressure measurements.

In Fig. 7, uncertainties in the measurements are indicated by arrows. If arrows indicating uncertainties in the values of α for O_2 and A had been shown in Fig. 1, the apparent inconsistency between low- and high-pressure measurements would be more readily understandable. It is evident from Table 11, and also Fig. 7, that the uncertainties increase at the lower pressures and become magnified at $p = 0$, where the highest accuracy is most desirable. The unbroken lines in Fig. 7 represent least squares equations based entirely on the measurements of Baxter and Starkweather, "weighted according to their probable errors" as stated in the 34th annual report[18] of the committee on atomic weights. The broken lines represent the 0 °C isothermal slopes or α's obtained in previous sections.*

Mean values for ρ_0 and values for RT_0 and M may be calculated from the measurements quoted in Table 11, as has been done by Baxter and Starkweather.[18] Similarly, values for ρ_0, RT_0 and M may be calculated using the values of α previously obtained. The differences in the calculated uncertainties in the two cases may be of interest.

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* The data on argon fall so close to the oxygen line in Fig. 7 that they were omitted to avoid confusion.

Equations (3.3) and (4.3), combined with $p = 0$, yield

$$pv = p_0 v_0(1 - \alpha) = \frac{RT_0}{M} \tag{13.1}$$

which may be written, for these calculations, in the equivalent forms

$$RT_0 = \frac{Mp_0(1 - \alpha)}{\rho_0} \tag{13.2}$$

$$M = \frac{\rho_0 RT_0}{p_0(1 - \alpha)} \tag{13.3}$$

Based entirely on the measurements of Baxter and Starkweather, the results turn out as follows:

$$RT_0 = \frac{32(1.00093 \pm 7)}{1.428965 \pm 10} = 22.4147 \pm 16$$

$$M(\mathrm{N_2}) = \frac{(1.25037 \pm 2)(22.4147 \pm 16)}{1.00041 \pm 9} = 28.0152 \pm 32$$

$$M(\mathrm{Ne}) = \frac{(0.89990 \pm 2)(22.4147 \pm 16)}{0.99941 \pm 16} = 20.1829 \pm 36$$

$$M(\mathrm{A}) = \frac{(1.78364 \pm 4)(22.4147 \pm 16)}{1.00089 \pm 12} = 39.9442 \pm 56$$

When the α's obtained from high-pressure measurements are used, the calculated uncertainties are reduced, as follows:

$$RT_0 = \frac{32(1.000951 \pm 9)}{1.428965 \pm 10} = 22.4151 \pm 3$$

$$M(\mathrm{N_2}) = \frac{(1.25039 \pm 2)(22.4151 \pm 3)}{1.000453 \pm 3} = 28.0149 \pm 6$$

$$M(\mathrm{Ne}) = \frac{(0.89990 \pm 2)(22.4151 \pm 3)}{0.99951 \pm 1} = 20.1812 \pm 6$$

$$M(\mathrm{A}) = \frac{(1.78364 \pm 4)(22.4151 \pm 3)}{1.00094 \pm 1} = 39.9430 \pm 11$$

For comparison, the 1940 international atomic weights give 28.016 for $\mathrm{N_2}$, 20.183 for Ne and 39.944 for A, the last two values apparently being based entirely on the measurements quoted in Table 11 When consideration is given to the results of other observers and different values are used for ρ_0 and the estimated uncertainty in ρ_0, the results are slightly different,* of course, but the major uncertainty in all published atomic weight calculations of this kind is in the value of α determined by low-pressure measurements alone.

It should be noted from Table 11 that the pressure unit is 760 mm Hg at 0 °C and $g = 980.616$. Expressing the above results for RT_0 in different units gives

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* Birge[2] used the same value of ρ_0 for $\mathrm{O_2}$. He used "least square probable error" apparently in his ± terms. Putting these on the basis used here (see section 5), his "adopted values" for ρ_0 and α lead to

$$RT_0 = \frac{32(1.000927 \pm 90)}{1.428965 \pm 90} = 22.4146 \pm 24 \text{ l mole}^{-1} \text{ atm } (g = 980.616)$$

22.4151 l mole^{-1} atm ($g = 980.616$)
22.4140 l mole^{-1} atm ($g = 980.665$)
22414.6 cm^3 mole^{-1} atm ($g = 980.665$)
2271.16 joules mole^{-1}

14. Conclusion

As a result of many careful and painstaking investigations in recent years, the slopes of the pv isotherms at 0 °C below two atmospheres for He, Ne, A, H_2, N_2, and O_2 appear to be known to about one per cent, which is comparable to a few parts in a million in relative measurements of pressure and volume at this temperature and in this pressure range. Reliable values for the isothermal slopes are of importance in atomic weight determinations, in gas thermometry, in certain theoretical calculations, in gas analyses, for example, in converting from volume per cent to mole per cent, and in many other applications where it is desired to avoid the approximations involved in the ideal gas laws.

Some of the summaries relative to these slopes, such as those given in "International Critical Tables," in the "Handbuch der Experimental Physik" and in the most recent summary by Keesom and Tuyn,[10] give the impression that these slopes are very uncertain because of the wide scatter in the published values obtained by different observers. It is hoped that the foregoing discussion of the subject may supply the key to some of the reasons for such a wide spread in the published values.

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The Location of the Normal Sulfur and Mercury Boiling Points on the Thermodynamic Temperature Scale*

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1. Introduction

Thermodynamic absolute temperature is that temperature which is implicitly defined by the empirical generalization and exact differential equation

$$dS = \frac{1}{T}dU + \frac{p}{T}dV, \tag{1}$$

expressing the first and second laws of thermodynamics. As such it is the temperature which must be used in all experimental investigations and calculations involving the second law. The establishment of this temperature is thus of importance for most physico-chemical measurements and for the many industries based upon them, in particular the steam power industry.

In thermodynamic theory, thermodynamic absolute temperature is usually defined explicitly as a function of the efficiency of a reversible heat engine and is thus independent of the physical properties of any specific substance. Theory also shows that the temperature so defined is identical with that of the ideal gas equation of state

$$(pV)_{\text{ideal}} = RT. \tag{2}$$

This provides the key to the practical experimental realization of thermodynamic temperature in the middle temperature range ($2° < T < 1500$ °K) since experience shows that at sufficiently low pressure the equation of state of any real gas is

$$pV = RT + Bp, \tag{3}$$

where B is a function of temperature only.

For the commonly used thermometric gases (helium, hydrogen, nitrogen) this equation is accurate to 1 in 100,000 at a pressure of 1 meter of mercury. Thus observation of the p,V,T properties of the fixed gases at pressures less than 1 meter of mercury serve to establish thermodynamic temperature. Traditionally these observations have been of two kinds, constant-volume and constant-pressure thermometry. In the constant-volume gas thermometer, the volume of a definite mass of gas is maintained constant and the pressure measured at each temperature; in the constant-pressure gas thermometer the pressure of a definite mass of gas is maintained constant and the volume measured at each temperature.

It only remains to assign a scale to the thermodynamic temperature so measured. This has been customarily effected for scientific work by making the interval from the freezing point to the boiling point of water 100 degrees (on the centigrade scale 0 and 100°, respectively). Recently Giauque[1] has proposed that the ice point be given a statutory value on the absolute thermodynamic scale, thus making the boiling point of water a constant to be determined.

Formulas derived from Equations (2) and (3) for reducing gas thermometer

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* Contribution of the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 435.

Table 1. Summary of Formulas for Reducing Gas Thermometer Measurements of Temperature to Temperature on the Thermodynamic Scale.[2]

Equation of State: $p_tV_t = RT + B_tp_t + \dots$

Thermodynamic Scale = Ideal Gas Scale	Constant-volume Gas Thermometer Scale	Constant-pressure Gas Thermometer Scale
$\alpha = \alpha_v - F_vp_0 = \alpha_p - F_pp_0$ ideal gas mean coefficient	$\alpha_v = \dfrac{(p_{100} - p_0)}{100p_0}$ mean coefficient of pressure increase	$\alpha_p = \dfrac{(V_{100} - V_0)}{100V_0}$ mean coefficient of expansion
$\dfrac{1}{\alpha} = T_0$ Kelvin temperature of ice point	$F_v = \dfrac{(1 + 100\alpha)(B_{100} - B_0)}{(100RT_0)}$	$F_p = \dfrac{[B_{100} - B_0(1 + 100\alpha)]}{(100RT_0)}$
$t = t_v + E_vp_0 = t_p + E_pp_0$ centigrade temperature	$t_v = \dfrac{100(p_t - p_0)}{(p_{100} - p_0)}$	$t_p = \dfrac{100(V_t - V_0)}{(V_{100} - V_0)}$
	$E_v = \dfrac{[t(T_0 + 100)(B_{100} - B_0) - 100(T_0 + t)(B_t - B_0)]}{(100RT_0)}$	$E_p = \dfrac{[t(B_{100} - B_0) - 100(B_t - B_0)]}{(100R)}$
$r = r_v + G_vp_0 = r_p + G_pp_0$	$r_v = \dfrac{p_0}{p_t}$	$r_p = \dfrac{V_0}{V_t}$
$t = \left(\dfrac{1}{r} - 1\right)T_0$	$G_v = \dfrac{(B_t - B_0)}{(RT)}$	$G_p = \dfrac{\left(\dfrac{B_tT_0}{T} - B_0\right)}{(RT)}$

measurements to temperature on the thermodynamic scale are summarized in Table 1.[2]

The gas thermometer is cumbersome to use and exacts refined experimental technique if accurate temperature measurements are to be made. For this reason it has been replaced in practice by a variety of simpler and more precise thermometers, for example, mercury-in-glass thermometers, electrical resistance thermometers and thermocouples. However, because of the necessity of using thermodynamic temperature in thermodynamic experiments and calculations it is desirable that the indications of the practical thermometers agree as closely as possible with the thermodynamic scale. A system for accomplishing this end within the then existing experimental error was adopted by the Seventh Conference of Weights and Measures in 1927[3] and is known as the International Temperature Scale.

The International Scale is based on a number of reproducible equilibrium temperatures (fixed points). Specifications are given for the establishment of the fixed points and numerical values assigned to them on the Thermodynamic Centigrade Scale. Temperatures intermediate to the fixed points are determined by standard interpolation thermometers. Specifications are given for the construction of the thermometers and definite formulas are given for the calculation of International temperatures from their indications.

In the middle range of temperature 0 to 660 °C the fixed points are the ice point (0 °C), steam point (100 °C) and sulfur point [444.6 °C (Int.)]. The interpolation instrument is the standard platinum resistance thermometers, and the interpolation formula is

$$\left(\frac{R_t - R_0}{R_{100} - R_0}\right)(100) + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) \quad \frac{R_t - R_0}{\alpha R_0} \quad \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) \qquad (4)$$

where $t = t$ °C (Int.).

Because of its practical and theoretical importance the relation of the International Scale to the Thermodynamic Scale has been studied in considerable detail at M. I. T. under the general supervision of Prof. J. A. Beattie. We have first studied the range 0 to 444.6 °C (Int.).

Four aspects of the problem have been investigated.

(1) The reproducibility and determinateness of the specified fixed points. The investigation of this aspect, including methods of measurement and establishment of the fixed points and their reproducibility and variation with external pressure has been previously reported.[4]

(2) The accuracy of the assigned numerical values for the fixed points on the Thermodynamic Centigrade Scale. A report on this aspect constitutes the greater part of this paper. Numerical values for the fixed points on the newly proposed thermodynamic scale[1] will also be given.

(3) The constancy and determinateness of the interpolation instrument. Definite methods of construction of platinum resistance thermometers have been described previously.[5] The constancy of the indication of a platinum resistance thermometer during routine use and the mutual agreement at temperatures intermediate to the fixed points of different platinum thermometers all satisfying the international convention will be given in this paper.

(4) The accuracy of the specified interpolation formulas. The work reported below shows that the international specifications for the construction of platinum resistance thermometers are so liberal that different platinum thermometers may disagree at intermediate temperatures by more than 0.01 °C and that none of them agrees with the Thermodynamic Scale within experimental error. Unpublished

work at M. I. T. in the range 0 to 444.6 °C and the work of others in the range −183 to 660 °C (the range covered by the platinum resistance thermometer according to the international convention) agree in showing that the International Scale is low from −183 to 0 °C and from 100 to 444.6 °C, and high from 0 to 100 °C and from 444.6 to 660 °C. Both the discrepancy between different platinum thermometers and their common deviation from the Thermodynamic Scale can be corrected within present experimental error by the inclusion of a cubic term in the relation between resistances and temperature.

$$= \left(\frac{R_t - R_0}{R_{100} - R_0}\right)(100) + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) + \gamma\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\left(\frac{t}{t_0} - 1\right). \qquad (5)$$

The inclusion of an additional term in the resistance temperature equation requires the establishment of an additional fixed point in this temperature range. It has been shown previously[4b] that the mercury boiling point is suitable for such a fourth fixed point.

This report contains data on the location of the normal sulfur and mercury boiling points on the Thermodynamic Temperature Scale, the location of the normal mercury boiling point on the International Temperature Scale and the variation of the latter from one platinum resistance thermometer to another. The degree of constancy of the M. I. T. platinum resistance thermometer over a period of several years is also recorded.

2. Outline of M. I. T. Experiments and Calculations[6]

The Thermodynamic Scale was realized by the use of two constant volume nitrogen gas thermometers. The International Scale was realized by four strain-free platinum resistance thermometers satisfying the International Convention and calibrated by the methods previously developed.[4] We used our own pressure-temperature formulas:

steam point

$$t = 100 + 0.0368578\,(p\text{-}760) - 0.000020159\,(p\text{-}760)^2 + 0.00000001621\,(p\text{-}760)^3 \qquad (6)$$

sulfur point

$$t = 444.6 + 0.0908028\,(p\text{-}760) - 0.000047573\,(p\text{-}760)^2 + 0.00000004361\,(p\text{-}760)^3 \qquad (7)$$

mercury point

$$t = 356.580 + 0.0730951\,(p\text{-}760) - 0.000039866\,(p\text{-}760)^2 + 0.00000003191\,(p\text{-}760)^3 \qquad (8)$$

but since we also used a controlled atmosphere constantly regulated within ±1 mm of 760 mm, this fact introduces no significant difference between our own platinum resistance thermometer scale and the International Scale.

The six thermometers were placed together in a well-stirred thermostat automatically regulated to ±0.001 °C and readings taken at 0, 25, 50, 75, 100, 150, 200, 250, 300 °C, mercury boiling point, 400 °C, and sulfur boiling point, the even temperatures being on the International Scale. From 0 to 150 °C an oil bath, and from 150 to 444.6 °C, a fused nitrate bath was used, readings in the two baths being related by duplicated readings at 150 °C.

The gas thermometer pressure ratios p_0/p_t were observed at each of the foregoing temperatures for ice-point pressures of .6, .45 and .333 meter of mercury. At each ice-point pressure, four separate pairs of sulfur-point readings were taken between two symmetrically spaced pairs of readings at 150 °C, and four single mercury-point readings between two pairs of readings at 150 °C. The ratios were extrapolated to zero pressure by least squares straight lines; B values derived from the slopes were smoothed as a function of temperature and the smoothed values used to calculate the thermodynamic temperature of each reading (Cf. Table 1). B values deduced from all available data by Professor Keyes[2] were also used in the reduction of the data.

All numerical values for thermodynamic temperatures cited later should be regarded as provisional, since a thorough treatment of our data is not yet completed. The values given will probably not be changed by as much as 0.01 °C on final calculation.

3. The Normal Sulfur Boiling Point

Table 2. Previous work[4a] has determined the reproducibility of the sulfur point as ±0.0016 °C. This is the probable error of a single determination in a series of determinations made in close time sequence under the same conditions. We have now studied twelve different platinum thermometers for periods of one to three years, making a total of 114 routine determinations of the sulfur point on ten different dates. The combined effect of reproducibility of the sulfur point and constancy of the platinum thermometers gives a probable error of a single determination of ±0.0035 °C. The agreement of these two figures shows that the sulfur point is a suitable fixed point and that the platinum thermometer is a suitable interpolation instrument as far as constancy goes.

Table 2. Constancy of Platinum Resistance Thermometers and Reproducibility of the Sulfur Boiling Point on the International Scale.

Calibration Number →	1	2	3	4	5	6	7	8	9	10
Date →	Sept. 1935	Dec. 1935	April 1936	June 1936	Sept. 1936	Oct. 1936	Dec. 1936	Feb. 1937	May 1937	June 1938

Thermometer (1)	Calibration Numbers (2)	Total Determinations (3)	Average δ (4)	Probable Error of Average δ (5)	Probable Error of Average (°C) (6)	Probable Error of Single Determination (°C) (7)
107	1, 2, 3, 4, 5, 6, 8	17	1.49267	±0.00005$_4$	±0.0008	±0.0034
306	2, 4, 5, 6, 7, 8	11	516	8$_7$	13	44
307	2, 3, 4, 5, 6, 7	14	371	4$_8$	7	28
308	1, 2, 3, 4, 5, 6, 7, 8	18	224	7$_3$	11	48
310	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	24	533	3$_6$	6	28
312	8, 9, 10	8	574	7$_7$	12	33
313	8, 9, 10	7	436	5$_7$	9	23
314	8, 9, 10	7	454	4$_6$	7	18
315	8	2	492			
316	8	2	480			
317	8	2	446			
318	8	2	438			
Ave.						±0.0035
Reproducibility of sulfur point[*]						±0.0016

[*] This is the probable error of a single determination computed from column (9) Table V, pp. 348-9, of J. A. Beattie, M. Benedict and B. E. Blaisdell, *Proc. Am. Acad. Arts Sci.*, **71**, 327-360 (1937).

Table 3 and Fig. 1. These compilations summarize the data available in the literature for the determination of the normal sulfur boiling point on the Thermodynamic Scale. The reductions to the Thermodynamic Scale have been made on a uniform basis, the numerical coefficients shown having been computed by means

Table 3. The Normal Sulfur Boiling Point on the Thermodynamic Scale from Gas Thermometer Measurements on Helium, Hydrogen, Nitrogen and Air during the Period 1890–1939 (Reduced to the Thermodynamic Scale by Means of the *B*-values of Keyes[2]).

Symbols and formulas used are given in Table 1

Reduction to the Thermodynamic Scale:

Gas	$10^7 F_v$ (°K⁻¹-meters Hg⁻¹)	$10^7 F_p$ (°K⁻¹-meters Hg⁻¹)	$10^4 E_v$ for $t = 444.6$ °C (°C-meters Hg⁻¹)	$10^4 E_p$ for $t = 444.6$ °C (°C-meters Hg⁻¹)
He	− 2.16	− 26.79	+ 221	− 8
H_2	+ 12.76	− 20.08	+ 427	+ 707
N_2	+132.12	+118.19	+1454	+6194

Author	Date	Thermometer	Gas	Boiling Point	p_0 (m Hg)	$10^7 \alpha_v$ or $10^7 \alpha_p$ as shown column 3	T_0 (obs) from column 7	t_v or t_p as shown column 3	t for T_0 (obs) column 8	t for $T_0 =$ 273.165[2]
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Callendar, Griffiths [7]	1891	const p	air	indirect	0.76	36751.2	272.767[a]	444.53	445.0[a]	
Chappuis, Harker [8]	1902	const V	N_2	indirect	0.529	36681.1	273.140	444.7[b]	444.8	444.8_4
Eumorfopoulos [9]	1908	const p	air	direct	0.767	36713.1	273.057[a]	444.45[c]	444.93[a]	
					0.762	36706.2	273.104[a]	444.55[c]	445.02[a]	
					0.760	36712.3	273.056[a]	444.78[c]	445.25[a]	
					0.753	36701.2	273.133[a]	444.60[c]	445.07[a]	
Holborn, Henning [10]	1911	const V	H_2	indirect	0.623	36624	273.092	444.51[d]	444.53	444.65
			He		0.613	36618				
Day, Sosman [11]	1912	const V	N_2	direct	0.502	36681[e]	273.114	444.45	444.52	444.60
Eumorfopoulos [12]	1914	const p	N_2	direct	0.792	36700.5	273.173	444.125[f]	444.616	444.603
					0.784	36701.9	273.155	444.140[f]	444.626	444.642
					0.757	36699.1	273.152	444.125[f]	444.594	444.615
					0.415	36658.7	273.152	444.356[f]	444.613	444.634
					0.395	36656.1	273.154	444.392[f]	444.637	444.655
Chappuis [13]	1917	const V	N_2	direct	0.564	36699	273.041	444.50	444.58	444.78
					0.562	36695.9	273.063	444.46	444.54	444.71
					0.553	36694.3	273.066	444.50	444.58	444.74
M. I. T. (Red Thermometer) [6]	1939	const V	N_2	indirect	0.600	36686.30	273.1712	444.6556	444.7428	444.7327
					0.450	36666.57	273.1704	444.6738	444.7392	444.7304
					0.333	36651.84	273.1656	444.6919	444.7403	444.7393
M. I. T. (Green Thermometer) [6]	1939	const V	N_2	indirect	0.600	36687.50	273.1628	444.6035	444.6907	444.6943
					0.450	36667.80	273.1621	444.6336	444.6990	444.7037
					0.334	36653.27	273.1559	444.6496	444.6982	444.7130
Average and probable error of average of all values rounded off to nearest 0.01 °C									444.64_4[a] $\pm 0.01_4$	444.69_2[a] $\pm 0.01_1$
Average and probable error of average of M. I. T. data									444.7184 ±0.0068	444.7189 ±0.0049

Notes:

[a] Accurate values for the reduction of air thermometer data to the thermodynamic scale are not available. The values for nitrogen were used to make approximate corrections. These values are not included in the average.

[b] The original value given for the S.B.P. is 445.2; this was corrected in a later paper by the use of new data on the thermal expansion of vitreous silica.

[c] The original values given for the S.B.P. are 0.97 °C lower than those listed here; correction by use of new data on the thermal expansion of vitreous silica was given by Callendar and Moss. The author omits 444.78 in his own average.

[d] The S.B.P. was determined by three platinum resistance thermometers calibrated against two others which in turn had been calibrated against the gas thermometers. The authors assume that the hydrogen and helium thermometers read on the Thermodynamic Scale.

[e] The author's measured value of $\alpha \times 10^7$ is 36685; the value they used is taken from Chappuis' data.

[f] The author's extrapolation was made by use of the values 444.125 °C and 444.356 °C.

of the formulas of Table 1 from *B* values given by Equations (21B), (22), and (25A) of Professor Keyes' paper.[2]

$$B_{\mathrm{He}} = 4.002[16.4873T^{-0.25} - 74.09T^{-0.75} - 24.6T^{-1.25}]\text{ml-mole}^{-1} \quad (9)$$

$$B_{\mathrm{H_2}} = 2.0156[60.000T^{-0.25} - 397.25T^{-0.75} - 2282.056T^{-1.25}]\text{ml-mole}^{-1} \quad (10)$$

$$B_{\mathrm{N_2}} = 28.016[10.08T^{-0.25} - 766.115T^{-1} - 1.7545 \times 10^{-8}T^{-4}]\text{ml-mole}^{-1} \quad (11)$$

and the values $R = 62.360$ ml-meters Hg-mole⁻¹ − °K⁻¹ and $T = 273.16$ °K. The determinations of the sulfur point have been of two kinds: direct, in which the gas thermometer bulb is immersed directly in condensing sulfur vapor; and indirect, in which the gas thermometer is compared in a thermostat with platinum resistance thermometers calibrated in the usual way at the sulfur point. The latter method is to be preferred because it gives the standard fixed point of the practical ther-

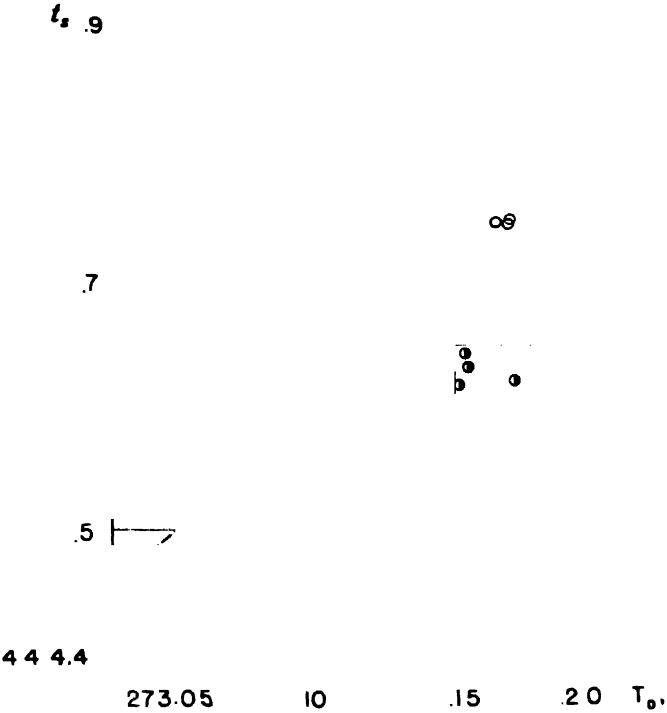

FIG. 1. Ordinate: normal sulfur boiling point on the Centigrade Thermodynamic Scale from gas thermometer measurements. Abscissa: ice point on the Kelvin scale observed with the same gas thermometer. The horizontal dotted line is the least squares fit of the data according to the usual definition of centigrade temperature, $1 \quad 1 \Big) T_{0_{\text{Observed}}}$. The sloping dotted line is the least squares fit of the data ording to Giauque's definition of centigrade temperature, $t = \left(\frac{1}{r} - 1\right) T_{0_{\text{Statutory}}}$.

⊖ Chappuis and Harker[8]
⊕ Chappuis[13]
⊖ Holborn and Henning[10]
⊕ Day and Sosman[11]
Eumorfopoulos[12]
○ M.I.T.[6] Red gas thermometer
● M.I.T.[6] Green gas thermometer

mometer on the Thermodynamic Scale. The temperatures of column (10) have been calculated according to the usual definition of centigrade temperature:

$$\left(\frac{p_t - p_0}{p_{100} - p_0}\right)_{\text{Ideal}} 100 = \left(\frac{p_t}{p_0} - 1\right)_{\text{Ideal}} T_{0_{\text{Obs}}} \qquad (12)$$

where $T_{0_{\text{Obs}}}$ is determined with the same gas thermometer as the other temperatures. The average of these values, each rounded off to the nearest 0.01 °C, is

444.64$_4$ °C, with a probable error of the average of ±0.01$_4$ °C. Because of the fact that the error in $T_{0_{\text{Obs}}}$ enters every temperature calculated according to Equation (12), and because the fractional effect of random error in the pressure on the constant factor T_0 is about three times the fractional effect on the variable ratio (p_t/p_0), Giauque has suggested that more consistent values of temperature can be obtained by using the definition

$$= \left(\frac{p_t}{p_0} - 1\right)_{\text{Ideal}} T_{0_{\text{Statutory}}} \tag{13}$$

where $T_{0_{\text{Statutory}}}$ is a suitable constant value arbitrarily taken for the Kelvin temperature of the ice point. The temperatures of column (11) have been computed from the latter definition for a T_0 of 273.165 °K, the value selected by Beattie [2]

$$t\,(\text{column } 11) = t\,(\text{column } 10) \times \frac{273.165}{T_0\,(\text{column } 8)}. \tag{14}$$

The average of these values each rounded off to the nearest 0.01 °C is 444.69$_2$ °C with a probable error of the average of ±0.01$_1$ °C, a slight decrease from the former value. In either case there are 16 degrees of freedom while the probable error of ±0.014 corresponds to a variance (s^2) of 0.00705625 and a ln s of -2.477, and the probable error of ±0.011 corresponds to an s^2 of 0.00429375 and a ln s of -2.725. This gives a z of 0.248, which shows that two samples of 17 each with a probable error of the average of ±0.014 and ±0.011, respectively, could easily be obtained by chance from a single parent population (probability is greater than 0.05); that is, that there is no statistically significant difference between the consistencies of temperatures calculated from the two definitions, Equations (12) and (13).[14] The failure to achieve the anticipated increase in consistency from the new definition for the temperature scale is undoubtedly due to the fact that the outstanding errors of gas thermometry are systematic errors charicteristic of the given instrument and affecting alike all measurements made with it. Apparently the definition Equation (12) has an advantage over the definition Equation (13), due to the elimination of the effect of all constant systematic errors in the pressure from the calculated temperature, which approximately compensates for the disadvantage of working with the small differences of larger observed quantities. The second definition Equation (13) has the serious disadvantage that it abandons the long-established centigrade base for practical thermometers and makes the steam point a value to be experimentally determined. The values furnished by Table 3 vary from 99.997 to 100.045 if T_0 is taken to be 273.165.

Table 4. This table summarizes our own results for the normal sulfur boiling point on the Thermodynamic Scale. The gas thermometer data were reduced to the Thermodynamic Scale in three ways. Keyes: the B values deduced by Keyes [2] were used (Equation 11 above). M.I.T. least squared: G_v was computed from the least squares straight line (r_v against p_0) through the three observed points at $p_0 = .6$, .45, and .33 meter of mercury. The two gas thermometers (Red and Green) were treated separately since they exhibited a systematic difference. M.I.T. smoothed: G_v values calculated as just described at each temperature observed were smoothed as a function of temperature. The results of Red and Green were averaged and fitted by least squares to the Keyes [2] type formula

$$(B_t - B_0)_{\text{mean}} = 20.86400 + 194.1198\,T^{-0.25} - 17684.13\,T^{-1} - 2.15691 \times 10^{10}\,T^{-4}\ \text{ml-mole}^{-1} \tag{15}$$

Table 4. The Normal Sulfur Boiling Point on the Thermodynamic Scale from Gas Thermometer Measurements on Nitrogen (M. I. T. Data).

Symbols and formulas used are given in Table 1.

Reductions to the Thermodynamic Scale

	Keyes	MIT least squared Red Thermometer	MIT least squared Green Thermometer	MIT smoothed Red Thermometer	MIT smoothed Green Thermometer
$10^9 G_v$ =	−773621	−761480	−736523	−760490	−742858

Red Gas Thermometer

		$-t_{SBP}$ for T_0 observed−			$-t_{SBP}$ for $T_0 = 273.16$−		
Reduction to Thermodynamic Scale ⟶		Keyes	MIT Least Squared	MIT Smoothed	Keyes	MIT Least Squared	MIT Smoothed
	$T_0^2 \rightarrow$	273.1663	273.1699	273.1683	273.165	273.165	273.165
p_0 (1)	r_v (2)	t_{SBP} (3)	t_{SBP} (4)	t_{SBP} (5)	t_{SBP} (6)	t_{SBP} (7)	t_{SBP} (8)
.6	.38004226	444.7349	444.7546	444.7531	444.7328	444.7466	444.7477
.45	.38016012	.7326	.7488	.7470	.7305	.7408	.7416
.333	.38024555	.7415	.7550	.7530	.7394	.7470	.7476
Ave.		444.7363	444.7528	444.7510	444.7342	444.7448	444.7456

Green Gas Thermometer

	$T_0^2 \rightarrow$	273.1608	273.1643	273.1628	273.165	273.165	273.165
p_0	r_v	t_{SBP}	t_{SBP}	t_{SBP}	t_{SBP}	t_{SBP}	t_{SBP}
.6	.38006224	444.6875	444.7352	444.7256	444.6943	444.7364	444.7292
.45	.38017396	.6969	.7342	.7263	.7038	.7353	.7299
.333	.38025870	.7062	.7353	.7289	.7131	.7365	.7325
Ave.		444.6969	444.7349	444.7269	444.7037	444.7361	444.7305

Average of Red and Green

444.7166	444.7438	444.7390	444.7190	444.7404	444.7381

Recommended value of the normal sulfur boiling point on the Thermodynamic Scale 444.7 °C

Red and Green were separated again by means of the relation

$$G_v \,(\text{Red}) = 1.023735\, G_v \,(\text{Green}) \tag{16}$$

Thermodynamic temperature was computed by the formula

$$= \left(\frac{1}{r} - 1\right) \tag{17}$$

Different determinations on a single gas thermometer showed a greatest difference of about 0.06 °C. The two gas thermometers differ systematically by about 0.03 °C. Different methods of reduction to the Thermodynamic Scale differ by about 0.03 °C. Taking into account all data we recommend for the normal sulfur boiling point on the Thermodynamic Centigrade Scale

444.7 °C.

4. The Normal Mercury Boiling Point

Table 5. Previous work[4b] has determined the reproducibility of the mercury point as ±0.00085 °C. This is the probable error of a single determination in a series of determinations made in close time sequence under the same conditions. We have now studied twelve different platinum thermometers for periods of one to three years, making a total of 83 routine determinations of the mercury boiling

point on seven different dates. The combined effect of reproducibility of the mercury point and constancy of the platinum thermometers gives a probable error of a single determination of ±0.0020 °C. The agreement of these two figures shows that the mercury point is a suitable fixed point and that the platinum thermometer is a suitable interpolation instrument as far as constancy goes. But the numerical values of the mercury boiling point are different for different thermometers, varying according to column (4) from 356.5690 to 356.5797 °C, a difference of 0.0107 °C.

Table 5. Constancy of Platinum Resistance Thermometers and Reproducibility of the Mercury Boiling Point on the International Scale.

Calibration Number →	1	2	3	4	5	6	7
Date →	Oct. 1935	Dec. 1935	Sept. 1936	Oct. 1936	Dec. 1936	Feb. 1937	May 1937

Thermometer (1)	Calibration Numbers (2)	Total Determinations (3)	356.5800 Minus Average Hg B.P. °C (Int.) (4)	Probable Error of Average (°C) (5)	Probable Error of Single Determination (°C) (6)
107	1, 2, 3, 4	11	0.0007	± 0.0006	± 0.0021
306	2, 4, 5	8	31	8	22
307	2, 3, 4, 5	8	17	9	27
308	1, 2, 3, 4, 5	15	3	2	7
310	1, 2, 3, 4, 5, 6, 7	18	46	6	27
312	6, 7	6	100	6	16
313	6, 7	6	57	4	10
314	6, 7	5	110	5	12
315	6	1	95		
316	6	1	65		
317	6	3	68	3	5
318	6	1	60		
Ave.			0.0039	± 0.0003	± 0.0020
Reproducibility of Mercury Boiling Point *					± 0.00085

* This is the probable error of a single determination computed from column (9), Table 3, pp. 381-2, of J. A. Beattie, B. E. Blaisdell, J. Kaminsky, *Proc. Am. Acad. Arts. Sci.*, 71, 375-385 (1937).

Table 6. The statistical significance of this variation is established in this table. The large values of z show that the probability of drawing by chance 12 samples which varied as much in their means as the values of column (4), Table 5, from a parent population in which the probable error of a single determination is

Table 6. Statistical Analysis of the Data of Table 5. [14]

	Sum of Squares	Degrees of Freedom	Variance		
Summation of the squares of the deviations of the 83 points from their common average	.0015544	82	.000018956		
This may be analyzed into the following parts:					
Variation between thermometers					
linear variation of $t_{\mathrm{HgB.P.°C(Int.)}}$ with δ	.0005049	1	.0005049	− 3.796	2.024
residual variation of $t_{\mathrm{HgB.P.°C(Int.)}}$ between thermometers	.0004237	10	.00004237	− 5.035	.785
Variation between measurements of $t_{\mathrm{HgB.P.°C(Int.)}}$ on a given thermometer	.0006258	71	.000008814	− 5.820	

±0.0020 °C is much less than .001, and further, that this variation may be separated into two parts, one part proportional to the value of δ of the thermometer and a second part not explicable in this way, and that the probability of chance occurrence of either part is likewise less than .001. This means the partial correlation of mercury boiling point with δ does not explain all the statistically significant variation between thermometers, although it is itself a statistically significant correlation. This shows that the International Scale is not adequately defined for reproducibility at temperatures between the fixed points and that a fourth fixed point such as the mercury point is necessary.

Table 7. The Normal Mercury Boiling Point from Measurements with the Platinum Resistance Thermometer During the Period 1890–1939.[a]

Author (1)	Date (2)	Method (3)	S. B. P. Used by Author (4)	δ Used by Author (5)	t (6)	t Corrected to S.B.P. = 444.6 (7)
Callendar, Griffiths[7]	1891	boiling tube	444.53	1.570	356.60	356.61
				1.786	.74	.75
				1.980	.82	.83
				1.859	.71	.72
				1.667–2.158	.74	.75
					.73	.74
Heycock, Lamplough[15]	1912	unspecified	444.53		.7	.7
Menzies[16]	1927	isotensiscope	444.60		.711	.711[b]
M. I. T.[6]	1939	boiling tube	444.60	1.492–1.496	.5761	.5761[c]

Notes:

[a] The formulas used in the calculation of temperature are those of the International Temperature Scale [Equation (4)], but the temperatures given are not in general on this International Temperature Scale because the platinum thermometers used do not satisfy the international specifications.

[b] The original data were given for a S. B. P. of 444.53. This was recomputed to a S.B.P. of 444.6 by Menzies in 1927.

[c] Detailed data for this entry are given in Table 5.

Table 7. This compilation summarizes the data available in the literature for the determination of the normal mercury boiling point on the platinum resistance thermometer scale. It will be noted that the data of Callendar and Griffiths likewise exhibit a variation of mercury boiling point with δ of the thermometer.

Fig. 2. This variation is shown graphically in the figure. The tabulated corrections of Waidner and Burgess[17] may be represented by the straight line (2),

$$\Delta t \quad - 1.3(\delta - 1.5). \qquad (17)$$

The observations of Callendar and Griffiths[7] may be represented by the least squares straight line (1),

$$\Delta t = 0.5075(\delta - 1.5) \qquad (18)$$

and those of M. I. T.[6] by the least squares straight line (3)

$$\Delta t = - 1.9466(\delta - 1.5). \qquad (19)$$

It can be seen that our results are in reasonable agreement with the table of Waidner and Burgess, but disagree with the results of Callendar and Griffiths. This disagreement is probably not experimental error, but is undoubtedly due to a real variation in the effect of impurity and method of construction upon the relation between temperature and δ for a platinum thermometer. That this is so is indicated by the fact that the M. I. T. data are not represented within experimental error by the straight line, Equation (19), (cf. Table 6) and that the mercury boiling point given by the data of M. I. T. and Callendar and Griffiths, respectively, are in essential agreement after correction to a common δ of 1.5 by the straight lines Equations (19) and (18) (cf. Table 8).

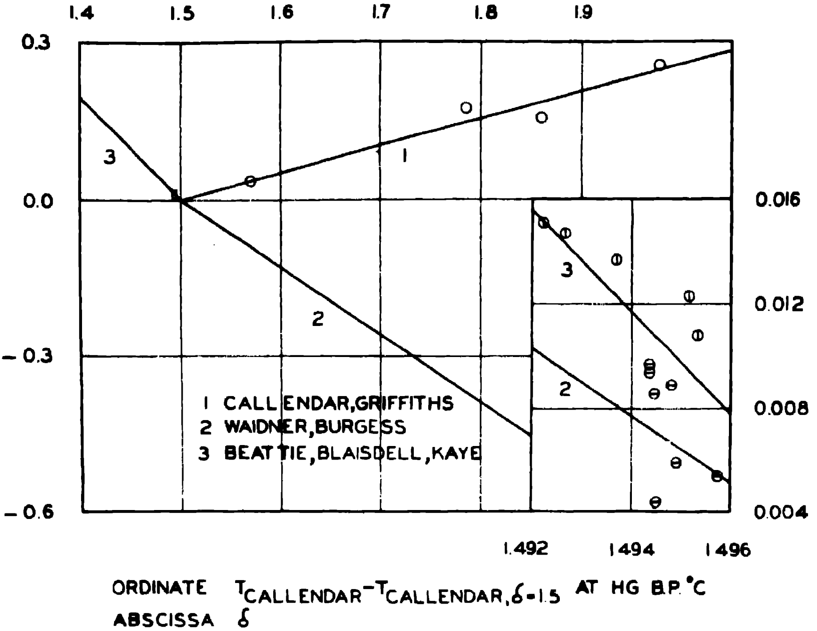

FIG. 2. Ordinate: normal mercury boiling point on a platinum resistance thermometer computed according to Callendar's equation minus the value obtained in a similar way from a platinum resistance thermometer of $\delta = 1.5$. Abscissa: δ. All the data of Beattie, Blaisdell and Kaye lie within the small rectangle near the origin which is repeated to enlarged scale in the lower right-hand corner.

⦶ Thermometers constructed prior to Jan., 1935.
⊖ Thermometers constructed in Jan., 1937.

Table 8. This table gives the results of these corrections applied to all the determinations of the mercury boiling point with platinum thermometers which have been reported in sufficient detail to permit correction. Such correction is necessary because the International Scale is inadequately defined at intermediate temperatures and does not give determinate values within easily attainable experi-

Table 8. The Normal Mercury Boiling Point on the International Scale Corrected to a δ of 1.5 from Measurements with the Platinum Resistance Thermometer during the Period 1890–1939.

Author	Hg B.P. °C (Int.) for $\delta = 1.5$
Callendar, Griffiths[7]	356.575
M. I. T.[8]	.5646
Recommended value of the normal mercury boiling point on the International Scale	356.57

mental error. We recommend for the normal boiling point on the International Scale

356.57 °C (Int.)

Table 9. This table summarizes the M. I. T. results for the normal mercury boiling point on the Thermodynamic Scale. There are no other results save those of Regnault[18] which are affected by a random error of more than 1 °C. The treatment of the data was as is described in Table 4. Different determinations on a single gas thermometer showed a greatest difference of about 0.025 °C. The two gas thermometers differ systematically by about 0.025 °C. Different methods of reduction to the Thermodynamic Scale differ by about 0.02 °C. We recommend for the normal mercury boiling point on the Thermodynamic Scale

356.7 °C.

Table 9. The Normal Mercury Boiling Point on the Thermodynamic Scale from Gas Thermometer Measurements on Nitrogen (M. I. T. Data).

Reductions to the Thermodynamic Scale.

	Keyes	MIT least squared Red Thermometer	MIT least squared Green Thermometer	MIT Smoothed Red Thermometer	MIT Smoothed Green Thermometer
$10^9 G_v$ ·	−821159	−821652	−780990	−808737	−789987

Red Gas Thermometer

Reduction to Thermodynamic Scale →		t_{HgBP} for T_0 observed			t_{HgBP} for $T_0 = 273.165$		
		Keyes	MIT Least Squared	MIT Smoothed	Keyes	MIT Least Squared	MIT Smoothed
T_0 →		273.1663	273.1699	273.1683	273.165	273.165	273.165
p_0 (1)	γ_v (2)	t_{HgBP} (3)	t_{HgBP} (4)	t_{HgBP} (5)	t_{HgBP} (6)	t_{HgBP} (7)	t_{HgBP} (8)
.6	.43318214	356.7118	356.7161	356.7253	356.7101	356.7097	356.7210
.45	.43330600	.7118	.7162	.7225	.7101	.7098	.7182
.333	.43340176	.7228	.7273	.7315	.7212	.7209	.7272
Ave.		356.7155	356.7199	356.7264	356.7138	356.7135	356.7221
		Green Gas Thermometer					
		273.1608	273.1643	273.1628	273.165	273.165	273.165
p_0	γ_v	t_{HgBP}	t_{HgBP}	t_{HgBP}	t_{HgBP}	t_{HgBP}	t_{HgBP}
.6	.43320378	356.6725	356.7122	356.7024	356.6780	356.7131	356.7053
.45	.43331968	.6843	.7151	.7072	.6897	.7160	.7101
.333	.43341236	.6991	.7231	.7168	.7045	.7240	.7197
Ave.		356.6853	356.7168	356.7088	356.6907	356.7177	356.7117
		Average of Red and Green					
		356.7004	356.7183	356.7176	356.7023	356.7156	356.7169
Recommended value of the normal mercury boiling point on the Thermodynamic Scale							356.7 °C

It will be noticed that there is a difference of 0.13 °C between the recommended values of the normal mercury boiling point on the Thermodynamic Scale and on the International Scale. About half of this difference can be absorbed by raising the International value of the sulfur point to the newly recommended thermodynamic value 444.7 °C. The remaining half shows that the International interpolation formula for the platinum thermometer is not adequate and that a fourth fixed point such as the mercury point is necessary. If the mercury point given above is adopted together with a cubic resistance-temperature relation in the Callendar form, Equation (5), the constant γ assumes a value of about -0.035, which effects agreement within present experimental error, between the Thermodynamic Scale and the International Scale throughout the range -183 to 660 °C covered by the platinum thermometer on the International Scale.

5. Summary

The importance of an accurate determination of the relation between the Thermodynamic Scale of temperature and the various practical scales is discussed.

A review of the literature and new experiments at M.I.T. lead to a recommendation of 444.7 °C for the normal sulfur boiling point on the Thermodynamic Scale and of the adoption of a cubic temperature-resistance relation as interpolation formula for the platinum resistance thermometer in the range 0 to 660 °C with the normal mercury boiling point at 356.7 °C on the Thermodynamic Scale as the additional fixed point.

On the present International Scale the normal mercury boiling point is 356.57 °C (Int.).

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A Practical Temperature Scale Below the Oxygen Point and A Survey of Fixed Points in This Range

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The methods used in measuring temperature have followed a more or less well-defined cycle. In a new range of temperatures the first measurements have been made with simple instruments on arbitrary temperature scales. Next, the more complicated gas thermometer has been set up and the thermodynamic temperatures of various fixed points determined. Finally, certain values of these fixed points have been accepted by general agreement, together with certain standard interpolation procedures, which have allowed the gas thermometer to be dispensed with and the simple instruments to be used once again. Above 83 °K (−190 °C) this cycle was completed in 1927 by the adoption of the International Temperature Scale. At lower temperatures there is as yet no general agreement on the thermodynamic temperatures of fixed points, or on the most satisfactory way of interpolating between them. Numerous laboratories have calibrated resistance thermometers and thermocouples by direct comparison with gas thermometers, but as yet no entirely satisfactory method of calibration based on fixed points alone has been proposed.

As a step toward the solution of this problem, the National Bureau of Standards has undertaken to maintain a provisional temperature scale* in the range 14 to 83 °K, based on a group of resistance thermometers (six Pt, one 90 Pt:10 Rh) calibrated by direct comparison with a constant-volume helium gas thermometer. The walls of the copper gas-thermometer bulb contained holes in which the resistance thermometers were placed. Gas-scale temperatures T_g were computed from the equation:

Table 1. Deviations for Correcting from the Helium Gas Scale (T_g) to the Thermodynamic (T).

[For $p_0 = 1$ m Hg]

T	$T-T_{0g}$	T	$T-T_{0g}$	T	$T-T_{0g}$	T	$T-T_{0g}$
10	+0.021	60	+0.002	120	-0.010	220	-0.021
15	+ .018	65	+ .001	130	- .012	230	- .021
20	+ .016	70	+ .000	140	- .013	240	- .022
25	+ .013	75	- .001	150	- .014	250	- .022
30	+ .011	80	- .002	160	- .015	260	- .023
35	+0.009	85	-0.003	170	-0.016	273.16	-0.023
40	+ .008	90	- .004	180	- .017	373.16	- .023
45	+ .006	95	- .005	190	- .018	—	—
50	+ .005	100	- 006	200	- .019	—	—
55	+ .004	110	- .008	210	- .020	—	—

$$T_g = C\left\{1 + f(T,p) + \frac{T_g}{V_0}\sum_i{}' \frac{V_i}{T_{gi}}\right\}p \qquad (1)$$

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* A complete report of the work summarized here has been given in reference 122.

Table 2. Resistance-Temperature Table Arranged for Linear Interpolation. Based on Platinum Thermometer *L6*.

[Linear interpolation yields temperatures correct to the nearest 0.001° above 19 °K, and correct to the equivalent of the nearest unit in the last figure of w below this temperature. $w = R/R_0$]

W	T	$\frac{\Delta T}{\Delta w}$
0.002800	10.090	7780
2850	10.479	7160
2900	10.837	6700
2950	11.172	6260
3000	11.485	5860
3050	11.778	5520
3100	12.054	5160
3150	12.312	4880
3200	12.556	4640
3250	12.788	4420
3300	13.009	4220
3350	13.220	4040
3400	13.422	3880
3450	13.616	3720
3500	13.802	3600
3550	13.982	3480
3600	14.156	3360
3650	14.324	3260
3700	14.487	3160
3750	14.645	3060
3800	14.798	2980
3850	14.947	2900
3900	15.092	2840
3950	15.234	2740
4000	15.371	2700
4050	15.506	2620
4100	15.637	2580
4150	15.766	2500
4200	15.891	
0.004200	15.891	2440
4300	16.135	2350
0.004400	16.370	2250
4500	16.595	2170
4600	16.812	2110
4700	17.023	2030
4800	17.226	1970
4900	17.423	1910
5000	17.614	1860
5100	17.800	1800
5200	17.980	1770
5300	18.157	1710
5400	18.328	1680
5500	18.496	1630
5600	18.659	1600
5700	18.819	1560
5800	18.975	1530
5900	19.128	1490
6000	19.277	1470
6100	19.424	1430
6200	19.567	1410
6300	19.708	1390
6400	19.847	1350
6500	19.982	1340
6600	20.116	1320
6700	20.248	1290
6800	20.377	1270
6900	20.504	1250
7000	20.629	1240
7100	20.753	1210
7200	20.874	1200
7300	20.994	1180
7400	21.112	1160
0.007500	21.228	1150
7600	21.343	1130
7700	21.456	1120
7800	21.568	1100
7900	21.678	1090
8000	21.787	1080
8100	21.895	1060
8200	22.001	1050
8300	22.106	1040
8400	22.210	1030
8500	22.313	1010
8600	22.414	1010
8700	22.515	990
8800	22.614	980
8900	22.712	970
9000	22.809	
0.009000	22.809	960
9200	23.001	935
9400	23.188	920
9600	23.372	905
9800	23.553	885
0.010000	23.730	870
.010200	23.904	855
.010400	24.075	840
.010600	24.243	830
.010800	24.409	815
.011000	24.572	805
.011200	24.733	790
.011400	24.891	780
.011600	25.047	770
.011800	25.201	760

Table 2.—(*Continued*)

W	*T*	$\frac{\Delta T}{\Delta w}$	*W*	*T*	$\frac{\Delta T}{\Delta w}$	*W*	*T*	$\frac{\Delta T}{\Delta w}$
0.012000	25.353	750	0.020000	30.287	518	0.036000	37.189	368
.012200	25.503	740	.020500	30.546	508	.036500	37.373	368
.012400	25.651	730	.021000	30.800	502	.037000	37.557	364
.012600	25.797	720	.021500	31.051	494	.037500	37.739	362
.012800	25.941	710	.022000	31.298	486	.038000	37.920	360
.013000	26.083	705	.022500	31.541	480	.038500	38.100	358
.013200	26.224	695	.023000	31.781	474	.039000	38.279	356
.013400	26.363	690	.023500	32.018	468	.039500	38.457	354
.013600	26.501	680	.024000	32.252	462	.040000	38.634	
.013800	26.637	670	.024500	32.483	456	0.040000	38.634	350
.014000	26.771		.025000	32.711	452	.041000	38.984	346
0.014000	26.771	663	.025500	32.937	444	.042000	39.330	342
.014300	26.970	653	.026000	33.159	440	.043000	39.672	339
.014600	27.166	643	.026500	33.379	436	.044000	40.011	335
.014900	27.359	637	.027000	33.597	432	.045000	40.346	332
.015200	27.550	623	.027500	33.813	426	.046000	40.678	329
.015500	27.737	617	.028000	34.026	422	.047000	41.007	326
.015800	27.922	607	.028500	34.237	418	.048000	41.333	323
.016100	28.104	600	.029000	34.446	414	.049000	41.656	320
.016400	28.284	593	.029500	34.653	410	.050000	41.976	318
.016700	28.462	587	.030000	34.858	408	.051000	42.294	314
.017000	28.638	577	.030500	35.062	402	.052000	42.608	313
.017300	28.811	570	.031000	35.263	400	.053000	42.921	310
.017600	28.982	567	.031500	35.463	396	.054000	43.231	307
.017900	29.152	557	.032000	35.661	392	.055000	43.538	306
.018200	29.319	553	.032500	35.857	390	.056000	43.844	303
.018500	29.485	547	.033000	36.052	386	.057000	44.147	301
.018800	29.649	540	.033500	36.245	382	.058000	44.448	300
.019100	29.811	533	.034000	36.436	380	.059000	44.748	297
.019400	29.971	530	.034500	36.626	378	.060000	45.045	296
.019700	30.130	523	.035000	36.815	376	.061000	45.341	293
.020000	30.287		.035500	37.003	372	.062000	45.634	292

Table 2.—(*Continued*)

W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$
0.063000	45.926	290	0.096000	54.859	255.0	0.148000	67.551	236.0
.064000	46.216	289	.098000	55.369	254.5	.150000	68.023	
.065000	46.505	287	.100000	55.878	252.5	0.150000	68.023	235.8
.066000	46.792	285	.102000	56.383	252.0	.155000	69.202	235.0
.067000	47.077	284	.104000	56.887	250.5	.160000	70.377	234.4
.068000	47.361	283	.106000	57.388	249.5	.165000	71.549	233.8
.069000	47.644	281	.108000	57.887	249.0	.170000	72.718	233.4
.070000	47.925	280	.110000	58.385	247.5	.175000	73.885	233.0
.071000	48.205	278	.112000	58.880	246.5	.180000	75.050	232.6
.072000	48.483	277	.114000	59.373	246.0	.185000	76.213	232.2
.073000	48.760	276	.116000	59.865	245.0	.190000	77.374	231.8
.074000	49.036	275	.118000	60.355	244.5	.195000	78.533	231.4
.075000	49.311	274	.120000	60.844	243.0	.200000	79.690	231.2
.076000	49.585	272	.122000	61.330	243.0	.205000	80.846	231.0
.077000	49.857	272	.124000	61.816	242.0	.210000	82.001	230.8
.078000	50.129	270	.126000	62.300	241.0	.215000	83.155	230.4
.079000	50.399	269	.128000	62.782	241.0	.220000	84.307	230.4
.080000	50.668		.130000	63.264	240.0	.225000	85.459	230.4
0.080000	50.668	268.0	.132000	63.744	239.5	.230000	86.611	230.2
.082000	51.204	266.0	.134000	64.223	239.0	.235000	87.762	230.2
.084000	51.736	264.0	.136000	64.701	238.5	.240000	88.913	230.4
.086000	52.264	262.5	.138000	65.178	238.0	.245000	90.065	230.8
.088000	52.789	261.0	.140000	65.654	237.5	.250000	91.219	230.8
.090000	53.311	259.5	.142000	66.129	237.5	.255000	92.373	231.0
.092000	53.830	258.0	.144000	66.604	237.0	.260000	93.528	231.2
.094000	54.346	256.5	.146000	67.078	236.5	.265000	94.684	

in which the second term in the braces compensates for the effect of temperature and pressure on the bulb volume, and the third term for the pressure-transmitting volume which cannot be maintained at the temperature of the bulb. Definitions of symbols are given in reference 122. For several reasons, chief of which was the high gas density employed (corresponding to $p_0 = 2.46$ m Hg), it was not feasible to determine the constant C in the orthodox manner by measurements at both the ice and steam points. Hence a value for T_g at the oxygen point was selected and used to obtain C. An important advantage of this procedure was that it allowed the new scale in the new range to join smoothly with the International

Temperature Scale. Since the latter is a centigrade scale, upon which the oxygen point is by definition −182.97 °C, it was necessary to convert this to an absolute temperature by selecting a value for the temperature of the ice point on the Kelvin scale. The value selected is 273.16 °K, which leads to an oxygen point of 90.19 °K. From this the correction $T - T_g$ was subtracted to obtain the value of T_g to be substituted into Equation (1).

The differences $T - T_g$ between the thermodynamic and the constant-volume helium gas scales were obtained from a study of published work. The available data were plotted and averaged graphically. The corrections obtained in this way are reproduced in Table 1. To obtain centigrade corrections $(t - t_g)$ from this table it is necessary only to subtract from each entry the value of $T_0 - T_{g0}$.

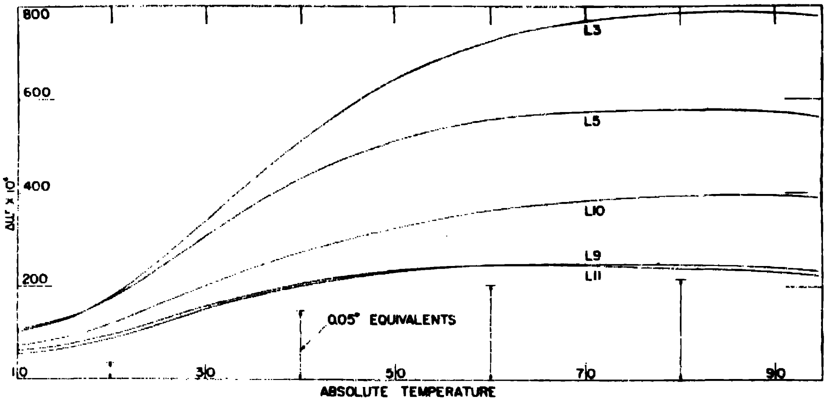

FIG. 1. Comparison of six calibrated platinum resistance thermometers.
$\Delta w_t = w_t - W_{L6}$ and $w = R/R_0$

From the results of simultaneous readings of the gas thermometer and the resistance thermometers, Table 2 was made up, giving the resistance-temperature relation for platinum. Since no two samples of platinum have exactly the same resistance-temperature relation, the table applies directly only to one particular thermometer. For other thermometers a deviation curve must be used, showing the difference between the particular thermometer and the standard table. A set of such deviation curves for some of our standard thermometers is shown in Fig. 1. For a more complete discussion of the experimental details and the computations the reader is referred to the original report.[122]

This provisional scale contains three fixed points: The boiling point of oxygen, which was discussed earlier, and the boiling and triple points of normal hydrogen. The last two were determined by direct experiment after the calibration had been completed. The values found were

boiling point	20.39 °K
triple point	13.96 °K

These three fixed points are too widely spaced to determine with the necessary accuracy a temperature scale employing platinum resistance thermometers, so for the present the scale must be considered as based on the resistances of the standard thermometers, with the three fixed points serving primarily as checks on their

Table 3. Published Values of the "Suitable" Fixed Points. Boiling Points are at $p = 760$ mm Hg Unless Otherwise Noted.

Year	Reference	t	T	(mm Hg)	Thermometer
	A, boiling point				
1895	Olszewski[9]	−186.9		740.5	H_2 gas
1901	Ramsay and Travers[19]	−186.1	86.90		Pt res
1913	Crommelin[34]	−185.84			Pt res
1915	Holst and Hamburger[41]		87.76	802.2	Pt res
1922	Born[54]		87.48		O_2, N_2 vap press
	A, triple point				
1895	Olszewski[9]	−189.6			H_2 gas
1901	Ramsay and Travers[19]	−187.9	85.1		Pt res
1913	Crommelin[34]	−189.30		515.65	Pt res
1915	Holst and Hamburger[41]		83.81	521.4	Pt res
1922	Born[54]		83.93	512.17	O_2, N_2 vap press
1928	Eucken and Hauck[63]		83.55		Pt res
1936	Clusius[102]		83.85	$516._3$	Pb res
	CF_4, triple point				
1930	Ruff and Keim[77]	−186.3	86.8		thermel[a]
1930	Lebeau and Damiens[76]	−191			CH_4 vap press
1932	Klemm and Henkel[89]	−186.8[b]			O_2 vap press
1933	Menzel and Mohry[92]	−183.6		<1	CH_4 vap press
1938	Eucken and Schröder[117]		89.47		Pb, Pt res
	CF_4, transition				
1938	Eucken and Schröder[117]		76.23		Pb, Pt res
	CO, boiling point				
1884	Wroblewski[3]	−186			thermel
1884	Olszewski[2]	−190.0			H_2 gas (?)
1885	Wroblewski[5]	−190		735	Cu-German silver thermel
1902	Baly and Donnan[20]		81.85[c]		H_2 gas const press
1913	Estreicher and Bobotek[36]	−192.02	81.01		He gas
1919	V. Winning[60]		81.66[d]		N_2, O_2 vap press
1929	Clusius and Teske[69]		81.62		N_2, O_2 vap press
1931	Verschoyle[85]	−191.47			Pt res
1931	Crommelin, Bijleveld, and Brown[79]	-191.47_5	81.61_9		Pt res
1932	Clayton and Giauque[86]		81.61		Cu-const[e] thermel
1932	Heuse and Otto[87]	−191.484			He gas const vol
	CO, triple point				
1884	Olszewski[2]	−211.0			H_2 gas (?)
1885	Olszewski[4]	−207		100	H_2 gas
1885	Wroblewski[5]	−199		90–100	Cu-German silver thermel
1913	Estreicher and Bobotek[36]	−205.70	67.33		He gas
1916	Eucken[45]		67.3		Pb res
1929	Clusius[66]		68.2_2		Pb res
1929	Clusius and Teske[69]		68.22		N_2, O_2 vap press

Notes:

[a] thermoelement, thermocouple, or thermopile. See paper by White, page 265.

[b] Contained ½% air.

[c] By linear interpolation in their smoothed table.

[d] As corrected by Clusius and Teske.[69] Original paper not available.

[e] Copper-constantan.

Table 3.—(*Continued*)

Year	Reference			(mm Hg)	Thermometer
	CO, triple point—(*Continued*)				
1931	Verschoyle[88]	−205.03[f]		114.86[f]	Pt res
1931	Crommelin, Bijleveld, and Brown[79]	−209.44	68.10	115.11[g]	Pt res
1932	Clayton and Giauque[86]		68.09	115.31	Cu-const thermel
	CO, transition				
1916	Eucken[45]		60.4		Pb res
1929	Clusius[66]		61.5_1		Pb res
1932	Clayton and Giauque[86]		61.55		Cu-const thermel
	C_2H_6, triple point				
1900	Ladenburg and Krügel[13, 15]	−172.1 and −171.4			thermel
1921	Maas and Wright[52]	−172.0			Pt res
1930	Wiebe, Hubbard, and Brevoort[78]	−183.65	89.52		thermels, Pt res
1937	Witt and Kemp[114]		89.87		Cu-const thermel
	C_3H_6, (propylene) triple point				
1921	Maas and Wright[52]	−185.2			Pt res
1931	Huffman, Parks, and Barmore[81]		88.2		Cu-const thermel
1939	Powell and Giauque[123]		87.85		Cu-const thermel
	C_3H_8, (propane) triple point				
1921	Timmermans[53]	−187.8			petroleum ether
1921	Maas and Wright[52]	−189.9			Pt res
1936	Hicks-Bruun and Bruun[104]	−187.1			5 junction thermel[h]
1938	Kemp and Egan[118]		85.45		Cu-const thermel
	H_2, "hydrogen"[i] boiling point				
1895	Olszewski[8]	−243.5			Pt res
1898	Dewar[11]	−238	35		Pt res
1899	Dewar[12]	−252	21		H_2 gas const vol
		. . .	35		Pt res
		. . .	27		90 Pt:10 Rh res
1901	Dewar[16]	−252.5	20.5		H_2, He gas const vol
1903	Travers, Senter, and Jaquerod[25]		20.41		He gas const vol
			20.22		H_2 gas const vol
1906	Kamerlingh Onnes and Braak[27]	−252.93[j]		(?)	H_2 gas const vol
1913	Kamerlingh Onnes and Keesom[37]	−252.76	20.33		Pt res
1914	PTR (Henning)[44]	−252.79			He gas const vol
1917	Cath and Kamerlingh Onnes[48]		20.39		He gas const vol
1921	Henning[51]	−252.80			He gas const vol
1922	Martinez and Kamerlingh Onnes[56]		20.35_2		res, He gas
1924	Henning and Heuse[57]	-252.78_9			He gas const vol
1927	Henning[61]	−252.77	20.43		He gas const vol
1931	Heuse and Otto[80]	−252.78			He gas const vol

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[f] By direct observation. The intersection of his two equations gives $T = 200.4$ °K, $p = 1749.4$ mm Hg. The equation for the liquid appears to be in error.

[g] 0.15146 atmosphere.

[h] Calibrated by the National Bureau of Standards.

[i] Bonhoeffer and Harteck[85] first prepared and investigated parahydrogen. Work done prior to this time may be assumed to be on normal hydrogen, but because of the tendency of this to change to parahydrogen at low temperatures, the composition of the hydrogen used in the earlier measurements must be regarded as uncertain.

[j] A barometer height (unreduced) of 761.2 mm Hg, with a mercury temperature of 14.9 °C apparently goes with this value.

Table 3.—(*Continued*)

Year	Reference			p (mm Hg)	Thermometer
	N_2, transition				
1916	Eucken [46]		35.5		Pb res
1916	Keesom and Kamerlingh Onnes [46]		35.3 to 36.4[ab]		Au res
1929	Clusius [64]		35.4		Pb res
1933	Giauque and Clayton [91]		35.61		Cu-const thermel
1935	Aoyama and Kanda [98]		35.4		Cu-const thermel
	Ne, boiling point				
1915	Kamerlingh Onnes and Crommelin [42]	−245.92			He gas const vol
1936	Henning and Otto [103]	−246.087[ac]	27.073[ac]		He gas const vol
	Ne, triple point				
1915	Kamerlingh Onnes and Crommelin [42]	−248.67		323.5	He gas const vol
1927	Crommelin and Gibson [68]	−248.52	24.57	323.5	Pt res
1929	Clusius [67]		24.59		Pb res
1936	Clusius [102]		24.5_1		Pb res
1936	Henning and Otto [103]	−248.60[ad]	24.56[ad]	325	He gas const vol
	O_2, boiling point				
1884	Wroblewski [3]	−184			thermel
1885	Olszewski [4]	−181.4			H_2 gas
1885	Wroblewski [5]	−181.5		740	Cu-German silver thermel
1888	Wroblewski [6]	−182.446		(?)	H_2 gas
1895	Olszewski [9]	−182.7			H_2 gas
1895	Estreicher [7]	−182.4[ae]			H_2 gas
1896	Olszewski [10]		90.60[af]		H_2, He gas
1900	Ladenburg and Krügel [13,15]	−182.05[ae]			thermel
1900	Baly [14]		90.96		H_2 gas const press
1901	Dewar [16]	−182.5			H_2, O_2, He gas const vol
1901	Holborn [18]	−182.7			H_2, N_2 gas const vol
1903	Travers, Senter, and Jaquerod [25]		{90.20 {90.10		He gas const vol H_2 gas const vol
1908	Kamerlingh Onnes and Braak [30]	−182.986[ag]			Pt res
1914	Henning [40]	-182.97_4			H_2 gas const vol
1918	Cath [49]	−182.95	90.14		He gas const vol
1922	Keyes, Townshend, and Young [55]	−182.94			H_2 gas const vol
1924	Henning and Heuse [57]	-183.00_4			He gas const vol
1927	Henning [61]	−182.99			Pt res
1927	Dodge and Davis [59]	−182.97			critical study
1927	Giauque, Johnston, and Kelley [60]	. . . .[ah]			Cu-const thermel
1929	Giauque and Johnston [70]		90.13		Cu-const thermel
1929	Keesom, van der Horst and Jansen [72]	−182.977			He gas const vol
1931	Heuse and Otto [80]	−182.962			He gas const vol
1932	Heuse and Otto [87]	−182.965			He gas const vol
1935	Aoyama and Kanda [97]	−182.98			H_2 gas const vol
1935	Keesom and Dammers [100]	-182.98_5			Pt res
1939	Hoge and Brickwedde [123]		90.19		critical study

[ab] Lower figure obtained on cooling, higher on heating.
[ac] See note p, page 148.
[ad] See note p, page 148.
[ae] Calculated by Travers, Senter, and Jaquerod.[25]
[af] Calculated by Baly.[14]
[ag] Reduction to the thermodynamic scale made by Keesom, van der Horst, and Jansen.[72]
[ah] Their data agree so well with those of Cath [49] that no new value was reported.

Table 3.—(*Continued*)

Year	Reference	t	T	p (mm Hg)	Thermometer
		O_2, triple point			
1903	Estreicher [23]	-226.98^{al}	46.05^{al}	0.9	He gas const vol
1911	Kamerlingh Onnes and Crommelin [33]	-218.4		~1	Pt res
1911	Dewar [31]		54	1.12	H_2 gas
1916	Eucken [45]		54.1		Pb res
1929	Clusius [66]		54.1		Pb res
1929	Giauque and Johnston [70]		54.39		Cu-const thermel
1931	Justi [82]		54.24	1.20	res
1935	Aoyama and Kanda [98]		54.4_0		Cu-const thermel
1935	Lisman and Keesom [101]		54.32_5		Pt res
1936	Henning and Otto [103]	-218.83^{aj}	54.33^{a}		He gas const vol
		O_2, transition^{ak} (43.8 °K)			
'16	Eucken [45]		42.5		Pb res
'29	Clusius [66]		43.5		Pb res
'29	Giauque and Johnston [70]		43.76		Cu-const thermel
'35	Aoyama and Kanda [98]		43.7_0		Cu-const thermel
		O_2, transition (23.7 °K)			
1916	Eucken [45]		23.5		Pb res
1929	Clusius [66]		23.8		Pb res
1929	Giauque and Johnston [70]		23.66		Cu-const thermel
		SiH_4, triple point			
1916	Stock and Somieski [47]	-185			pentane
1933	Clusius [90]		88.48		Pb res
		SiH_4, transition^{al}			
1933	Clusius [90]		63.45		Pb res

[al] In 1913 Estreicher [35] says that, as suggested by Wahl,[39] he may have confused the triple point with the transition lying about 10 degrees lower.

[aj] See note *p*, page 148.

[ak] According to Wahl [39] oxygen becomes viscous and glassy before it freezes, but breaks up into small crystals at the 43.8 °K transition. This may explain why Justi [82] found the transition sharper on heating than on cooling.

[al] This transition may not be sharp enough for thermometric work.

constancy. As the necessary experimental work can be carried out, however, it is planned to establish other fixed points on the scale, spaced closely enough together so that the fixed points rather than the standard thermometers may ultimately serve to define the scale. The question of suitable fixed points is discussed in a subsequent section of this paper.

Apparatus has been set up for the calibration of thermometers on this provisional temperature scale, and a few calibrations have already been made, both on resistance thermometers and on thermocouples. Calibration of a resistance thermometer consists of determining for it a deviation curve such as those shown in Fig. 1. The temperature interval between calibration points is determined by the accuracy of the calibration desired. Since the calibration consists entirely of resistance measurements, the precision with which a single point may be determined is equivalent to one or two thousandths of a degree. This is the precision of the comparison with the standards, however, and should not be confused with the accuracy with which the standard thermometers themselves reproduce the thermodynamic scale. This latter uncertainty is much larger, but it is hoped that

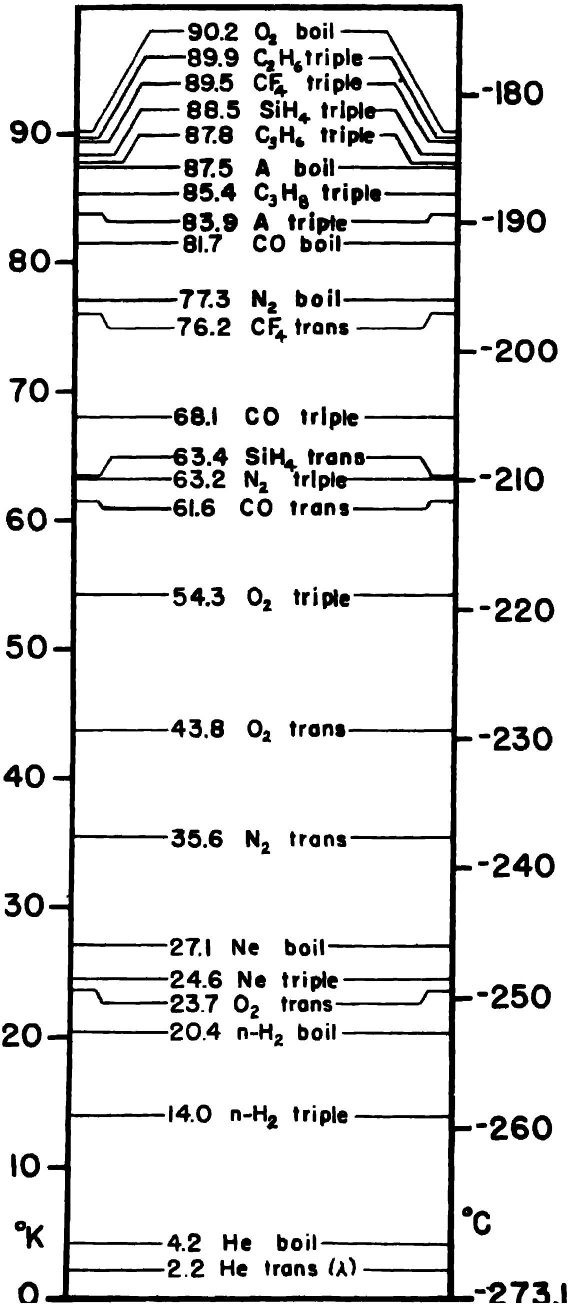

FIG. 2. "Suitable" fixed points below the oxygen point. Values have been rounded off to the nearest 0.1 degree. For more accurate values Table 3 should be consulted. All the points of this table are shown in the figure except the boiling and triple points of p-H_2, which lie slightly below the corresponding points of n-H_2.

the gas thermometry was sufficiently accurate so that the scale of the standard thermometers is everywhere within 0.02 degree of the thermodynamic scale.

It is evident that a standard thermometer is useful only so long as it retains its calibration. All the standard thermometers were very carefully annealed, and numerous intercomparisons and checks of resistance at fixed points have revealed no significant changes over a period of more than three years.

Survey of Fixed Points

As a preliminary to the establishment of further fixed points on the provisional temperature scale, a survey of published work on fixed points was made. The results of this survey, which covers the temperature interval from the oxygen point downward, are presented in the tables and discussion which follow. The points are divided somewhat arbitrarily into two groups, referred to as "suitable" and

Table 4. "Unsuitable" Fixed Points.
The term *fixed point* is used somewhat loosely. The table contains some transitions not sufficiently definite or sharp to qualify as fixed points in the ordinary sense.

Point	T	Reference	Reason "unsuitable"
HBr trans	89.62	116	hysteresis
CD_4 triple	89.4	115	purity[a]
PH_3 trans	88.10	113	
OF boil	87.8	94	corrosive
F_2 boil	85.21	93	corrosive
CH_4-C_2H_4 eutectic	84.55	106	
H_2Se trans	$82._3$	110	not sharp, hysteresis
HI trans	70.12	71	not sharp
NF_3 triple	64.7[b]	95	
$NiCl_2$ trans	57–58	107	hysteresis
NF_3 trans	54[b]	95	
N_2-O_2 eutectic	50.1	105	
F_2 triple	50[b]	24	corrosive
OF triple	50[b]	94	corrosive
PH_3 trans	49.43	113	
$NiCl_2$ trans	49.6	107	
OF_2 triple	49.4[b]	84	
OF trans	47[b]	94	corrosive
OF trans	38[b]	94	corrosive
PH_3 trans	30.29	113	
AsH_3 trans	20.5 to 32.1	108	
CD_4 trans	26.95	115	purity,[a] not sharp
$CoCl_2$ trans	24.9	107	
n-D_2 boil	23.59	99	purity[a]
e-D_2 boil	23.53_8[c,d]	99	purity[a]
$FeCl_2$ trans	23.3	107	
CH_3D trans	22.6	108	purity,[a] not sharp
HD boil	22.13_4[d]	120	purity[a]
CD_4 trans	21.90	115	purity,[a] not sharp
CH_4 trans	20.4	108	not sharp
n-D_2 triple	18.71	99	purity[a]
e-D_2 triple	18.67[c,d]	99	purity[a]
$CrCl_2$ trans	16.8	107	
HD triple	16.60_4	120	purity[a]
CH_3D trans	15.5	108	purity,[a] not sharp

Notes:

[a] *Purity* indicates that the substance has been found difficult either to prepare or keep in pure form. However, recent work of Brickwedde and Scott (unpublished) indicates that in the case of deuterium compounds these difficulties are not greatly different from those met with in preparing other pure substances.

[b] Converted with $T_0 = 273.16$ °K.

[c] *Ortho-para* equilibrium at 20.4 °K (97.8% *ortho*, 2.2% *para*).

[d] Computed from the extrapolated vapor pressure equation.

"unsuitable." It is very probable that further experimental work will show some of the "suitable" points to be actually unsuitable for use as low-temperature fixed points, and an occasional "unsuitable" point may find its way into the other group, but a rough classification based on present knowledge seemed desirable. Superconducting transitions have not been included in the survey.

The "suitable" fixed points were examined exhaustively in an attempt to include all values reported up to the present time. The results of this study are given in Table 3. Each value of temperature given has been transcribed literally from the author's report. This accounts for the appearance of values in °C in some cases, of values in °K in others, and of values on both scales in still others, and also for the several different values of the absolute temperature of the ice point which result. Except as noted, each reference given in the table was directly examined, and checked for references to earlier work. The more recent abstract journals and survey articles[103, 121] were also consulted. It is hoped that no major investigation has been overlooked, and that such omissions as may be found are chiefly preliminary reports, republications in other languages, or revisions. The arrangement of the substances whose fixed points are given is alphabetic in the chemical symbols. The positions of the "suitable" fixed points on the temperature scale are shown in Fig. 2. All the points included in Table 3 are shown, with the exception that for hydrogen only the normal modification ($n - H_2$) is included.

No attempt was made to treat the "unsuitable" points with the same thoroughness. They are listed in Table 4. Where more than one reference had been located the more recent one is given.

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Chapter 2
Precision Thermometry

Reproducibility of the Ice Point

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The ice point is commonly defined as the temperature at which ice and water are in equilibrium at normal pressure. In 1926 Foote and Leopold[1] pointed out that in the laboratory ice baths are prepared in such a way that the equilibrium temperature of ice, water, and air at barometric pressure is actually obtained. They pointed out that the presence of the air lowered the temperature by 0.0023 °C, and suggested changing the definition of the ice point to take into account the dissolved air. When the present International Temperature Scale was adopted in 1927 this was done, the ice point being defined[2] as the "Temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure."

As a result of the paper by Foote and Leopold and the change in the definition of the ice point, there seems to have arisen a rather common belief that the ice point cannot be realized to better than 0.002 to 0.003 °C. This, however, is far from being true. As Foote and Leopold pointed out, air is taken up very rapidly by the water and it is difficult to prevent the water from becoming fairly well saturated with air.

In 1927 Michels and Coeterier[3] investigated the triple point of water and suggested its use instead of the ice point as a fundamental fixed point to realize the temperature scale. Their investigation was conducted by means of a resistance thermometer, and the triple point was found to be reproducible to better than 0.001° C. A more careful investigation was made by Moser[4] in 1929 at the Physikalisch-Technische Reichsanstalt, also using a resistance thermometer method, and he reported the temperature of the triple point to be definite to about 0.00005 °C. He also advocated the use of the triple point instead of the ice point in defining the temperature scale.

From an academic point of view the triple point appears to be better than the usual ice point for fixing a point on the temperature scale. However, an ice bath is so much easier to prepare and use that it will be used by the experimenter in preference to a triple-point apparatus unless he is forced to change by the need for greater precision. It therefore seems worth while to consider the status of our information on the reproducibility of the ice point.

In 1932 the National Bureau of Standards decided to build some electrical resistance standards of pure metals[5] if a temperature could be found which was sufficiently reproducible. To allow measurements of resistance to a part in a million, a temperature which was definite to 0.0002 or 0.0003 °C was required. To test the suitability of the ice point for this purpose, a 10-ohm copper resistance coil was mounted in a double-walled container and arranged so that its resistance could be measured with the precision Thomson double bridge of the Resistance Section of the National Bureau of Standards. The resistance of this coil was measured in six separate ice baths, the measurements extending over a period of five days. During this short time the resistance of the copper coil as well as that of the manganin standard with which it was compared probably remained constant. The spread in the resistance measurements was one part in a million, corresponding to a spread in temperature of 0.00025 °C. On the basis of these results some pure-metal 1-ohm standards were constructed and measured frequently over a period of five months.

Assuming that the standards changed in resistance at a uniform rate, and attributing the erratic variations entirely to differences in ice-bath temperatures, the results indicated a reproduction in the temperature to about 0.0002 °C.

As a further test of the reproducibility of the ice point as it is realized in practice, a triple-point apparatus [6] was prepared, and the difference between the triple point and the temperature of the ice baths was measured. A series of 20 measurements, involving nine separate ice baths and two separate fillings of the triple-point container, was taken over a period of nearly two months. Only one measurement differed from the average value of 0.0097 °C by more than 0.0001 °C. The spread in values obtained was about what would result from changes in barometric pressure, although no correlation was found between the pressure and the observed temperature differences. The average barometric pressure during these measurements was about 75 cm of mercury. As the temperature of the ice baths is lowered by 0.0001 °C by an increase in pressure of 1 cm of mercury, the experimentally determined difference corresponds to a difference of 0.0098 °C between the temperature of the triple point and of the ice point. This difference is exactly that obtained by Moser [4] from a measurement of the effect of pressure combined with a calculated value for the effect of dissolved air.

These results indicate that the ice point is reproducible to about 0.0001 °C if correction is applied for pressure. It must be remembered that the pressure below the surface of the liquid in the ice bath is increased by about 2 cm of mercury for each foot of immersion.

Recently Beattie, Huang and Benedict [7] repeated these measurements on the difference between the temperature of the ice point and the triple point. Although they applied corrections for pressure and for the conductivity of the water in both baths they arrived at the same value for the temperature difference, *i.e.*, 0.0098 °C, with about the same spread in the values obtained as in the previous work. [6] It is difficult to appraise the reliability of their results, as they made no mention of the apparatus which was used in measuring the emf of the thermocouples which were used to measure temperature differences. A measurement to 0.0001 °C required that the emf of their 50-junction thermocouple be determined to 0.2 microvolt, and this is far from a routine determination. In spite of the lack of information on the electrical measurements, this paper indicates careful work on the part of the experimenters, and considerable reliance must be put on their conclusions that the ice point is reproducible to about 0.0001 °C.

Additional evidence of the accuracy of reproduction of the ice point has been furnished by White,[8] who made "cold cells," which were ice baths in which the water could be drawn off and replaced with a fresh supply. He found that pairs of these cells would give the same temperature to 0.0001 °C or better, and that they would remain together in temperature for several days, provided that the water was replaced occasionally with air-saturated distilled water.

It would seem to be a fair summary of our present information to say that the ordinary ice point and the triple point are realizable to about the same accuracy, that is, to about 0.0001 °C. Besides the investigations which have been made on the ice point or the triple point individually, three investigations have independently given a difference in temperature between the two points of 0.0098 °C. The consistency in this measured difference is further proof of the reproducibility of both temperatures. When once set up, the triple-point apparatus will give a temperature which is independent of barometric changes. This probably is the best argument for the use of this temperature in the definition of the temperature scale. However, it requires special apparatus and extreme care in its use, as temperature changes in the inside tube in which the thermometer is inserted are not quickly compensated by melting or freezing in the bath proper. From the point of view of the experimenter a good ice bath is easily prepared and used, and furnishes the more satisfactory fixed point for the temperature scale. An important result of investigations of the triple point has been a demonstration of the excellence of the ice point.

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Precision Resistance Thermometry

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1. Introduction

The resistance thermometer as an instrument for the precise measurement of temperature had its beginning with the publication in 1887 of H. L. Callendar's[1] paper "On the Practical Measurement of Temperature." Callendar, in this paper or shortly afterward,[2, 3, 4] described the essential elements required in precise resistance thermometry, namely, a resistor properly mounted and protected, a means for measuring its resistance, and a relation between resistance and temperature. Subsequent developments have consisted largely of refinements and improvements in detail.

The situation when Callendar began his work was discouraging enough. In 1871, C. W. Siemens, in a Bakerian lecture before the Royal Society of London, had outlined a method of temperature measurement by means of the platinum resistance thermometer or pyrometer.[5] This pyrometer was investigated by a Committee of the British Association, who reported in 1874[6] that their experiments showed that in the form made by Siemens the resistance suffered large changes after the instrument had been heated to high temperatures. Among the members of the committee were Sir W. Thomson, Clerk Maxwell, G. C. Foster, Fleeming Jenkin, and C. W. Siemens. Apparently most of the work was done by two students, Charles Law and O. J. Lodge. While this list of names may not have been as impressive at the time as it sounds now, the report was sufficiently discouraging to deter anyone having adequate respect for authority from reopening the subject. Detailed examination of the report and of Siemens' later paper,[7] suggest that the report was the product of unskilled labor.

Two questions of terminology may well be disposed of at the outset. It is undoubtedly true that the term "resistance thermometer" logically means the ensemble of resistor, the means for connecting it to the resistance measuring equipment, the resistance measuring equipment itself and its accessories, such as battery, galvanometer and galvanometer reading device. There is very little occasion to use a single term to describe the ensemble, and the term "resistance thermometer" has come to mean the resistor itself and the other things permanently fastened to it, such as protecting tube and connecting leads. On the basis that good usage is essentially a compilation of the mistakes habitually made by the right people, the term "resistance thermometer" will here be used with what has become its customary meaning. Similarly, and for the same reasons, the term "resistance measurement" will be used instead of the more logical "resistance comparison."

2. The Resistance Thermometer

A resistance thermometer for general use consists of the resistor, a framework for supporting it, a protecting tube or sheath, connecting wires extending from the ends of the resistor to the top of the enclosure, and a means of securing the connecting wires at the top of the protecting tube and of joining them to flexible leads which are used to make the connections to the resistance measuring apparatus.

In special cases some of the elements may be omitted, so that a thermometer designed to be built into other equipment may consist merely of the resistor, supporting framework, protection, and terminals to which connections may be made.

Precise resistance thermometry for over fifty years has meant, almost without exception, platinum resistance thermometry. Various reasons are assigned for choosing platinum, among these that it is a noble metal, meaning that it is more or less indifferent to its environment, that it is easily workable, and that refining and manufacturing have been perfected until it is one of the most reproducible of materials. An outstanding reason for the choice of platinum is, however, that the relation between resistance and temperature is an exceedingly simple one, which holds over a very large range of temperatures. The relation between resistance and temperature, which is purely empirical, is one of the few examples of such a relation which, with the passing of time, has been found to be even better than was supposed when the relation was first announced.

The platinum is ordinarily used in the form of wire. Depending upon the purpose for which the thermometer is designed, the wire may be as small as 0.05 mm in diameter or, in exceptional cases, as small as 0.02 mm or as large as 0.6 mm in diameter, the latter if the thermometer is designed for use at temperatures as high as 1000 or 1100 °C. The resistance at 0 °C may be as large as several hundred ohms, or as small as a tenth of an ohm. However, for general use, the preferred type is made of wire 0.1 mm in diameter adjusted to have a resistance at 0 °C of about 25.5 ohms, so that the resistance changes by about 0.1 ohm per degree centigrade. About two meters of wire are required. For many purposes a thermometer made of wire 0.15 or 0.2 mm in diameter and adjusted to have a resistance at 0 °C of about 2.55 ohms is very convenient. Thermometers of this kind were used extensively in the earlier work in resistance thermometry.

Platinum wire of the requisite purity is now readily obtainable from a number of sources. Wire which has proved entirely satisfactory has been purchased under the following simple specification:

"Platinum wire, highest purity, surface smooth and free from defects, hard drawn, (.. mm diameter), on spool. The wire to be drawn from an ingot which has been completely fused, not from forged sponge.

"Test for purity: A sample of the wire will be annealed and the electrical resistance at 0 and 100 °C will be determined. The ratio R_{100}/R_0 must be greater than 1.391.

"Test for character of metal: When an end of the wire is melted in a flame, it must melt quietly without sputtering, scintillations, or other evidence of evolution of volatile matter."

It is preferable to order the wire hard-drawn as, for some purposes, it is more easily handled in this condition and can easily be annealed if desired. In making the test for purity, a suitable length of the wire may be annealed sufficiently for the purpose by passing enough current through it to heat it to redness. The heating should be continued for a few minutes. The lower limit for R_{100}/R_0 may be specified as 1.3915 or possibly 1.392 if desired, although the latter is near the attainable upper limit which is about 1.3925. Wire drawn from forged sponge will not meet the "test for character of metal."

The wire is formed into a coil which must be mounted on some sort of framework to hold it in position. The ideal mounting is one that leaves the wire as free as possible from mechanical constraints, so that dimensional changes resulting from thermal expansion shall impose a minimum of mechanical stress on the platinum. Other requirements are that the mounting shall be such that the thermometer will not have excessive time lag, and that the heating effect of the measuring current shall not be excessive. The platinum must not be in contact with materials which may contaminate it.

Callendar almost from the beginning used mica strips to support the coil, and later used the now familiar frame made of two strips of mica joined to form a cross, with notches cut into the edges of the strips to hold the wire in place. This type of mounting was first described by Heycock and Neville,[8] who used thermometers made by the Cambridge Scientific Instrument Company, but they attribute the design to Callendar. This mounting resulted in a minimum of contact between the wire and other solid materials, but did involve the possibility of subjecting the wire to strain. A great deal of ingenuity has since been expended in modifying Callendar's basic design so as to reduce the tendency to strain the wire. The modifications have consisted essentially in winding the wire so that the individual turns are circular in form rather than square, and pass through holes or slots in the mica rather than being wound into notches. With this construction, the wire is permitted a small amount of motion relative to the mica, but the possible motion is limited so that the coil retains its shape. Details of construction are given in papers by Sligh[9] and by Beattie.[10] With constructions of the type described a thermometer, made of wire 0.1 mm in diameter and having a resistance at 0 °C of about 25 ohms, will require a protecting tube which may be as small as 9 mm or as large as 15 mm in outside diameter. Coil lengths are usually in the range from 6 to 12 cm.

When an especially compact form is desired, the construction described by Meyers[11] may be used. The wire is first wound into a fine helix, and this helix is then wound, as if it were a wire, on a mica cross. With this construction a 25-ohm resistor of 0.1 mm-wire can be accommodated in a protecting tube not over 8 mm outside diameter, with a coil length of about 2 cm. A thermometer of these dimensions is very convenient, as it can be used in spaces no larger than those required to accommodate an ordinary mercury-in-glass thermometer.

Protecting tubes may be of glass, porcelain, fused silica, or metal. It is advisable to use a protecting tube not less than 40 cm long, except in special cases, and lengths greater than 40 cm are necessary or desirable in many instances. The tube may be filled with dry air under a pressure of $\frac{1}{3}$ to $\frac{1}{2}$ atmosphere at room temperature. The oxidizing atmosphere is an advantage.

In addition to the standard form of resistance thermometer described above, a special form designed for calorimetry[9] has been used to a considerable extent. In this form the platinum wire is wound on a flat strip of mica; and this strip, with mica insulating strips on each side, is inserted into a flattened metal sheath. This type of thermometer has the advantage of small time lag, the importance of which is easily overestimated. Its principal advantage appears to be its larger current-carrying capacity, that is, it will carry a given current with much less heating of the wire than will thermometers of the usual type. Its chief disadvantage is that it is more subject to changes of resistance resulting from such things as a slight bending and subsequent straightening of the sheath. It is therefore less suitable than the better protected types of thermometers for general temperature measurements, but it has proved extremely satisfactory for calorimetric work, where a change of temperature occurring in a relatively short period of time has to be measured with high precision.

For the connecting wires inside the protection tube, gold has been found very satisfactory. It is cheap, easily worked, inert, of suitable resistivity, and has a low thermoelectric power against copper.

The lead wires from the protected enclosure at the top of the protecting tube may be single copper wires of appropriate size. Since such wires may be rather stiff, several smaller wires in parallel may be used for each lead. A very useful form is made of No. 26 (0.4-mm) silk-insulated wire, three of which, again wrapped with silk, form one lead. Four of these strands, covered with a silk braid, serve to make the connections from the thermometer head to the resistance-measuring equipment. The length of such leads is ordinarily in the range from 2 to 4 meters, although much greater lengths are used on occasion. Lamp cord should not be used, as breakage of even one strand would make the resistance of the cord variable.

Resistance thermometers suitable for precise laboratory work are now available from manufacturers of instruments, so that further detailed descriptions are unnecessary here. Such detailed descriptions may be found in references 9, 10 and 11.

Callendar's first measurements were made with an ordinary Wheatstone bridge, so that the measured resistance included that of the connecting leads as well as that of the coil. He at first short-circuited the leads at the coil and thus measured their resistance, but he very soon used a pair of leads similar to those connected to the coil, which were measured separately, and their resistance was then subtracted from the measured resistance of the coil and its leads. Shortly afterward Callendar connected the dummy leads in the variable arm of the bridge,[2] adjacent to the thermometer arm and introduced a slide wire between these two arms. In this case the two arms had to be equal, and the subtraction was then performed automatically. These features were incorporated in the Callendar-Griffiths bridge described by Griffiths.[12] This last step made it impossible to use the bridge with the Siemens 3 lead,[5] or with the four terminal types of resistor. Callendar accordingly continued to use the type of compensated leads which he originated.

The Callendar type of thermometer with a pair of compensating leads was the most important type for some 25 years after 1887, and is still described in textbooks. Later the advantages of the four-terminal type of resistor, with current and potential terminals, led to its general adoption for precise work, and the compensated types were reserved for industrial uses. The determination of the properties of steam by Egerton and Callendar [13] in 1932 may have been the last important research in which the compensated type of thermometer served for the temperature measurements.

The statement is found occasionally that, with the type of thermometer having compensating leads, heat flow along the leads will be without effect on the measured resistance, since any effect in one bridge arm is compensated by an equal effect in the adjacent arm. The argument may be very misleading if it is taken to show that the compensated types have an advantage over the four-terminal type, as this is not true. The temperature of the end of the compensating loop of a Callendar type thermometer, the branch point of a Siemens type, or the two branch points of a four-terminal type, must all be unaffected by lead conduction if the measured resistance of the thermometer is to correspond to the temperature of the medium in which the thermometer is immersed. It is for this reason that the gold leads of a four-terminal thermometer are not carried down to the branch points. In the preferred construction a two- or three-cm length of platinum wire, preferably of the same diameter as that of the coil, is interposed between the branch point and the gold lead wire.

It has been claimed that the Callendar type of thermometer is especially adapted for differential measurements, such as those required in flow calorimetry, since two thermometers may be so connected in adjacent arms of a Wheatstone bridge that the difference of their resistances may be measured directly. In extended-flow calorimeter measurements at the National Bureau of Standards in 1922,[14] arrangements were made to control conditions sufficiently well so that the two thermometers could be read separately, without sacrifice of reliability of measurement. In fact, if conditions had been so unsatisfactory that direct reading of the difference in the resistances of the thermometers had been necessary, the accuracy of the results would necessarily have suffered. The much greater reliability of the four-terminal type of thermometer, which is not dependent upon any assumptions concerning the permanence of lead resistance, more than compensates for the greater ease of reading which may be obtained with differential thermometers of the Callendar type. If a direct determination of the temperature difference by means of a single observation is required, the thermel (thermocouple) would appear to be the most appropriate instrument.

The experiments of Laby and Hercus[15] on the mechanical equivalent of heat may have been among the last precise measurements made with thermometers of the Callendar type, differentially connected to measure the temperature difference in a flow calorimeter.

3. Measurement of Resistance

The characteristics of platinum are such that, in order to attain an accuracy of 0.001 °C in temperature measurement, except at low temperatures, a precision of resistance measurement of two to four parts in a million is required. The determination of a temperature depends upon the evaluation of a change or a difference in resistance, for example, the difference between the resistance of a thermometer at the temperature to be measured, and its resistance at the ice point, or again, the change in the resistance of a thermometer used in a calorimeter. In calorimetric measurements a precision of measurement of two to four parts in ten million may be required. Since the accuracy of the temperature measurement depends upon the accuracy with which a change of resistance is determined, the accuracy required in the resistance measurement, as distinguished from the precision, depends upon the circumstances, and generalizations are difficult to make. Accuracy in terms of any particular standard is never necessary, since all that is required is that resistances be determined in terms of a standard that is invariable over certain periods of time. For general use, equipment capable of a precision of the order of one part in a million is almost necessary, and the accuracy must be such that the differences of any two resistances, each observed to 1 part in a million, shall have real significance.

The measurement of the resistance between the branch points of a resistor having current and potential terminals involves two operations as a minimum. All the operations may be direct observations, or one or more of the observations may be replaced by an adjustment of resistance.

The resistance measurements may be made by a variety of methods, among which are the potentiometer method, the Thomson (popularly known as the Kelvin) double-bridge method, the Wheatstone bridge method, the Carey-Foster bridge method and the differential galvanometer method. The use of the two last named is rapidly acquiring the status of one of the lost arts, and references to papers describing the methods will be omitted here, lest someone be tempted to revive them.

In the potentiometer method, a standard resistor of the four-terminal type and the resistance thermometer are connected in series with a battery. Measurements of the potential drops across the two resistors, which carry the same current, then yield directly the ratio of the two resistances. In using the potentiometer method, a standard cell is not necessary; in fact it is better not to use one. The current through the thermometer should be adjusted to a suitable value, and the current through the potentiometer should then be so adjusted that readings of the desired accuracy can be obtained. Since the potential drop across a resistance thermometer is usually not over 0.1 volt, a low-voltage type of potentiometer, with a circuit designed to eliminate the effects of stray electromotive forces, should be used. Potentiometers of this type have not been made with more than five decades; consequently to attain a precision of one part in a million, even when readings are made to 0.1 of a step of the lowest decade, it is necessary that readings be made near the upper limit of the range of the instrument. The measurement of the potential drop across the standard resistor and of that across the thermometer constitute the minimum number of operations required for a resistance measurement. In addition, to eliminate the effects of stray electromotive forces, the measurements should be repeated with both the potentiometer current and the current through the resistors reversed in direction. Any change in the stray electromotive forces, if it occurs between the two measurements, will introduce a corresponding error.

The potentiometer method is capable of as high a sensitivity as the other methods, but is in general less convenient to use. The potentiometer with its five decades is not as well adapted to the purpose as the bridges in use, which are made with six decades. The potentiometer has an advantage when the resistance to be measured varies over a wide range, as is the case when a thermometer having a resistance at 0 °C of 25 ohms is used at liquid hydrogen temperatures, where its resistance may be less than 0.1 ohm. At the low resistances the desired precision may be easily obtained with the potentiometer by using a standard resistor of suitable resistance, and adjusting the measuring current. Thus the advantage of the potentiometer is that the percentage precision of measurement may be kept nearly the same over a large range of resistance, whereas with the bridge measurements the precision is in general to a certain fraction of an ohm for all resistances.

A further advantage of the potentiometer is that it is a much more versatile instrument than a bridge, and has many uses other than that of measuring resistance.

Two forms of the Thomson double bridge especially suited for resistance thermometry have been described by F. E. Smith.[16] In the one in use at the National Physical Laboratory and described by Hall,[17] the fixed arms have a 100 to 1 ratio, and the main variable arm has approximately 100 times the resistance of the thermometer. One of the auxiliary bridge arms is fixed while the other is variable, and the switches controlling the main variable arm are mechanically connected to those controlling the auxiliary variable arm, so that the two variable arms change together. The circuit has been very ingeniously designed so that, if three of the lead resistances of the thermometer are adjusted to equality, the resistance between the branch points of the thermometer is found from one balance of the bridge. The bridge is made with six decades, and its range is from 0 to 111 ohms. The effects of variations in switch contact resistances are of little importance, since all the contacts are in series with relatively large resistances.

In the Smith bridge, four operations are required for the measurement of a resistance between branch points. Three of these operations consist of adjusting the resistances of the leads of the thermometer, and are done once for all. The bridge has therefore the outstanding advantage that only a single reading is required for a measurement. Its disadvantages are that it requires 120 coils for its six decades, which must be of the double type, and that the battery voltage must be varied approximately in the same proportion as the measured resistance, if the measuring current through the thermometer is to be kept constant. The NPL bridge is provided with an 80-volt battery. The adjustment of the lead resistances is rather critical, and equality within a few per cent at all temperatures may be necessary.

The potentiometer and the Thomson bridge methods have been treated rather briefly because they are not used extensively, at least in this country. The choice of method appears to be largely a matter of longitude, the Thomson bridge being preferred in the longitude of Greenwich, the potentiometer east of Greenwich, and the Wheatstone bridge west of Greenwich.

The resistance of a four-terminal conductor can be measured very simply with a Wheatstone bridge by making two observations. The method was apparently first described by F. E. Smith[16] and has been used in a number of variations, one of the simplest of which[18] is illustrated by Fig. 1. The equal ratio arms are marked r_1 and r_2. R_a and R_b are the resistances required to balance the bridge in Figs. 1A and 1B respectively. X is the resistance between the branch points of the thermometer, and the leads are designated C, c, t, and T.

From Fig. 1A: $R_a + C = X + T$
From Fig. 1B: $R_b + T = X + C$

Adding yields $X = \dfrac{R_a + R_b}{2}$

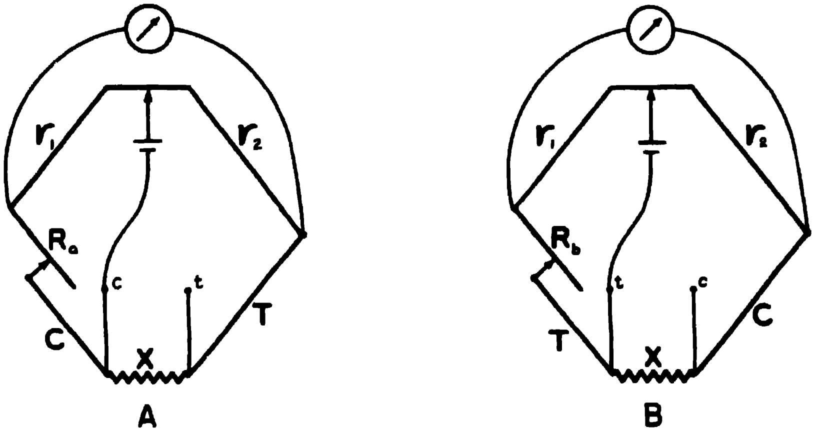

FIG. 1. Circuit diagrams to illustrate the method of measuring the resistance of a four-terminal conductor by the Wheatstone bridge method.

The ratio arms r_1 and r_2 may be adjusted to equality, within one or two parts in ten million, by means of the slide wire between them. In practice, the change from the connections of Fig. 1A to those of Fig. 1B is made by means of a commutator with amalgamated contacts. In principle, the commutator is equivalent to a three-pole, double-throw switch.

In the type of bridge[18] with which this method is generally used, the variable resistance is made up of six decades, having steps of 10, 1, 0.1, 0.01, 0.001, and 0.0001 ohms respectively. In the usual arrangement, the three decades of lowest resistance are Waidner-Wolff elements,[19] the 1-ohm and 0.1-ohm decades are movable branch-point elements,[19] the movable points being in the equal high-resistance ratio arms, and the 10-ohm decade is connected in the variable arm in the ordinary way by means of a plug or with amalgamated contacts. Eppley[20] has used a modified arrangement, in which the four lower decades are Waidner-Wolff elements and the 10-ohm and 1-ohm decades are movable branch-point elements. A brief comparison of the two will be attempted here.

The most important advantage of Eppley's arrangement is that all of the six decades may be made with conventional dial switches, whereas the older arrangement works best with amalgamated contacts in the 10-ohm decade. To offset this advantage, Eppley's arrangement requires that the resistances of the variable arm and the thermometer arm be not less than 10 ohms each, even when the resistance to be measured is zero. Also, unless special provision is made, the resistance in the galvanometer circuit will always exceed 100 ohms.

It is apparent that the differences between the two arrangements are of minor importance, that either one will serve for any purpose for which the other is suitable, and that the choice between the two will be largely determined by personal preference, and perhaps to some extent by the kind of measurements to be made.

A number of accessories may conveniently be built into the bridge. In addition to the slide wire between the ratio coils and the means for interchanging these coils, which are really integral parts of the bridge, these accessories include:

(1) The commutator already described, with provision for determining the "bridge zero."
(2) A resistor variable over a range of a few hundredths of an ohm, which may be connected in series with one of the thermometer leads, and adjusted so that the two balances of the bridge with the commutator in its two positions will be very nearly the same.
(3) A damping resistor variable from 0 to about 400 ohms and a double-pole, double-throw switch to connect it either in series or in parallel with the galvanometer.
(4) A milliameter in the battery circuit, graduated 0 to 5 milliamperes, and indicating the current through the thermometer, which is one-half of the current flowing through the instrument.
(5) Variable rheostats and keys in the battery circuit.
(6) A separate circuit, connected by inserting a plug into a receptacle, to form a complete bridge for conveniently checking or adjusting the equality of the ratio arms.

When making resistance measurements to a precision of one part in a million, the temperature of the bridge coils becomes important. In the range of room temperatures, the resistance of manganin coils is represented very well by the equation

$$R_t = R_{25}\cdot[1 + a(t - 25) - 0.0000004(t - 25)^2]$$

The value of the constant a may be zero or negative, but for most coils it is positive, and it may be as large as 0.000050. Even if the manganin is selected, it is not safe to assume that a is smaller than 0.000010. If the value of a for a coil is 0.000010, its temperature coefficient, according to the preceding formula, will have the following values.

Temp. °C	Temp. Coefficient $\frac{1}{R}\frac{dR}{dt}$
20	0.000014
25	.000010
30	.000006
35	.000002
37.5	.000000

At temperatures above 37.5 °C, the temperature coefficient will be negative. The average coefficient between 20 and 35 °C is 8 parts in a million per degree centigrade.

It is possible, in principle, to determine the temperature coefficients of the various coils in a bridge, and, knowing their temperature at the time measurements are made, to calculate their resistances. This has rarely been done consistently, since it is much more convenient to maintain the coils at a constant temperature. This has usually been done by immersing the coils in a stirred, thermally controlled oil bath. Recently another device has been used, which involves mounting all coils having a resistance of 0.1 ohm or more (a little more than one-half of the coils in a bridge) in an aluminum block, which in turn is placed inside of, and thermally insulated from, a thermally controlled aluminum box. The box is insulated with balsa wood, and an expenditure of from 2 to 4 watts serves to maintain the coils at 35 °C under conditions ordinarily encountered in a laboratory. Even if failure of the thermoregulator should leave the heating current on continuously, the temperature of the coils would not rise more than about 20 °C above room temperature.

Bridges of the types described are now listed in manufacturers' catalogs, so that there is no need to describe them in greater detail.

The recent development of the gold-chromium resistance alloy provides the possibility,[21] not yet realized, of using a material having a temperature coefficient so small that, within the ordinary range of room temperatures, the resistances of the coils will not change by more than 1 or 2 parts in a million. The gold-chromium alloy need not be used for coils corresponding to steps of less than 0.1 ohm.

From time to time when using a bridge, there is an opportunity to measure a resistance with two combinations of coils, for example, a resistance slightly greater than 30 ohms may be measured, first with the first three ten-ohm coils in circuit, and again with the first two ten-ohm coils and the ten one-ohm coils in the circuit. Such a pair of measurements will yield a relation between the resistance of the third ten-ohm coil and the sum of the ten one-ohm coils. If such measurements are made systematically, requiring some 50 pairs of measurements in all, the data obtained are sufficient for calibration of the bridge. The algebra of reducing the observations is very simple, and need not be repeated here, as it is available elsewhere,[18] or may be worked out independently by anyone who is interested. By making an additional measurement, for example of a 10-ohm standard resistor in terms of the ten one-ohm coils, the resistances of all the coils may be expressed in terms of the unit in which the resistance of the 10-ohm standard is expressed.

The point to be emphasized here is that it is far simpler for the user of a bridge to make the calibrations himself than it is to pack it up and send it to another laboratory for calibration. The calibration so made will be far more valuable than a vicarious one, since it will give the user a fair idea of the reliability of his measurements. The calibration should be repeated at intervals of about 6 months, until sufficient data have been accumulated on the stability of the coils to indicate how frequently calibration is necessary. If the measurements are made at intervals of exactly 6 months, seasonal changes may be missed, so that intervals of 4, 5, or 7 months may be better. Seasonal changes in resistance coils are known to occur, although modern coils are much better in this respect than those of 30 years ago.

As the use of resistance thermometers has increased, more and more occasions have arisen for making measurements with a number of thermometers, in rapid succession, using a single bridge. A selector to accomplish this was described many years ago.[18] An improvement on this was described by Eppley.[20] The most useful form, however, is that described by Beattie and his associates.[10,28] In principle, their selector is a four-pole, multiple-throw switch, preferably made with amalgamated contacts for the sake of compactness and convenience. The form described by Beattie was somewhat awkward mechanically, but this is not necessary. The selector may include devices for adjusting the resistances of the C and T lead resistances of each thermometer to approximate equality.

4. Relations between Resistance and Temperature

For temperatures above 0 °C, the original Callendar formula[1]

$$t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

has as yet no serious competitor. In this formula t is the temperature in degrees centigrade, R_t is the resistance of the platinum resistor at temperature t, R_0 and R_{100} are its resistances at 0 and 100 °C respectively, and δ is a constant characteristic of the individual thermometer to be determined by calibration of the thermometer at some fixed point, preferably the boiling point of sulfur. The value of δ may be expected to be between 1.49 and 1.50 °C. When the formula was first used by Callendar, he considered it correct within about 1 °C in the range 0 to 500 °C. Later investigations, some by indirect methods, such as the measurements of Heycock and Neville[8] and of Waidner and Burgess[22] of the temperatures of fixed points such as boiling points and melting points, and numerous comparisons of resistance thermometers with gas thermometers, have only served to show that gas thermometry in the range from 0 to 630 °C is not yet sufficiently precise to determine that the formula is inadequate.

Among the gas thermometer investigations which have contributed to establishing the validity of the Callendar equation are those of Callendar himself[1] and those of Chappuis and Harker[23] (corrected later by Chappuis[24]), Holborn and Henning,[25,26] and Henning and Heuse.[27]

More recently Beattie and his associates[28] announced, in advance of the publication of their work in detail, that their measurements serve to establish a distinct though very small difference between temperatures calculated from the Callendar formula with constants determined by calibration at 0 °C, 100 °C and the boiling point of sulfur, and temperatures on the thermodynamic centigrade scale. In the writer's opinion, the differences they announced are no larger than the possible, as distinguished from the probable or even the estimated limiting errors of gas thermometry, though it may be conceded that they have probably determined the direction of the departures.

It is of course inevitable that the Callendar formula will ultimately fail to meet all requirements, if the accuracy of gas thermometry becomes much higher than that prevailing at present. It is also possible that with platinum not of the highest purity, the Callendar formula may yield a better approximation to the thermodynamic scale than it would if the platinum were entirely pure. Certainly, at the present time, any belief that platinum of the highest attainable purity will define a scale which conforms more closely than slightly less pure platinum, is not warranted by the available data.

It has long been known that in the range below 0 °C, the Callendar formula held fairly well down to −40 or −50 °C, but failed to reproduce the thermodynamic scale at lower temperatures. The formula proposed by Van Dusen[29]

$$t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left(\frac{t}{100} - 1\right) \frac{t}{100} + \beta \left(\frac{t}{100} - 1\right) \frac{t^3}{100^3}$$

represented the available data[30,31] at the time it was published (1925) very satisfactorily. The constants R_0, R_{100} and δ are determined by calibrations at 0 °C, 100 °C, and the boiling point of sulfur, and the constant β is then determined by a calibration at the boiling point of oxygen.

The validity of the formula has been strenuously[32] and exhaustively[33] attacked by Keesom. In his earlier work,[32] a difference of nearly 0.1 °C was found between the temperatures defined by two resistance thermometers at −78 °C, and the temperature defined by one of the thermometers differed from the temperature on the thermodynamic scale by over 0.2 °C. In later work by Keesom and Dammers [34,35] after the technique had been learned, the differences between the scales defined by different resistance thermometers became as small as would normally be expected, and the difference between the resistance thermometer scale and the thermodynamic scale decreased to a few hundredths of a degree. Their values for the differences between the two scales are in good agreement as to order of magnitude with those of Heuse and Otto,[36] but are not in full agreement in regard to the signs of the differences.

The form of the difference curves found by Keesom and Dammers is not such as to inspire confidence. Differences between two functions, such as the temperature calculated by the Van Dusen formula, and the temperature on the Kelvin scale when plotted against the temperature, simply do not exhibit sharp corners. The form of these difference curves, no less than the abnormal values of the constant δ found in Keesom's earlier work,[32] was an unheeded warning of the presence of systematic errors. These are among the reasons why an important problem of low-temperature thermometry is the further test of the validity of the Van Dusen formula, or the development of a better one.

Moser [37] has proposed a modification of the Callendar formula to provide a resistance thermometer scale which will agree better with the thermodynamic scale at high temperatures, up to the gold point (1063 °C). This work still requires independent verification.

5. Measuring Current and Galvanometer Sensitivity

The power dissipated in the thermometer coil by the measuring current is in most cases less than 1 milliwatt. With the small power it is evident that to make observations of resistance precise to 1 part in a million or better, a very sensitive galvanometer is required. An analysis of the galvanometer problem is beyond the scope of this paper, and it will suffice to mention those characteristics of a galvanometer which determine its suitability for use in measuring resistances. These characteristics are (1) the complete period, (2) the external resistance requisite for critical damping, (3) the deflection in millimeters, at a scale distance of one meter, produced by an emf of 1 microvolt with the critical damping resistance in series, (4) the size and quality of the mirror, (5) freedom from thermoelectromotive forces originating in the galvanometer itself, (6) freedom from zero drift, and (7) insensitivity to mechanical disturbances.

A considerable proportion of the galvanometers used in resistance thermometry at the National Bureau of Standards have approximately the following characteristics. Complete period, 5 seconds, critical damping resistance, 50 ohms, sensitivity, 5 mm per microvolt with the critical resistance in series, plane mirror ⅜ inch (1 cm) in diameter. With an "all copper" circuit, thermoelectromotive forces cause little or no inconvenience, the zero is fairly good, and in most of the buildings special protection against vibration is not necessary.

Recently galvanometers having about the same period and critical damping resistance and a sensitivity of 10 mm per microvolt have become available. When a longer period is permissible higher sensitivities may be obtained.

It will be noted that nothing has been said about coil resistance. The choice of this should be left to the designer of the galvanometer, to enable him to meet the requirements which are important.

With galvanometers of the general type described, working sensitivities from 1 to 20 mm per 0.001 °C are obtained, depending upon such factors as scale distance, measuring current, etc.

The measuring current which may be used depends on circumstances. For the flat sheath calorimetric thermometers the standard measuring current is 5 m. a. through the thermometer (10 m. a. through the bridge). For thermometers of the types mounted in tubes, the standard measuring current is 2 m. a. for a thermometer having a resistance of 25 ohms at 0 °C, and 4 m. a. for a thermometer having a resistance of 2.5 ohms at 0 °C. With these currents the heating of the resistor by the measuring current is a few thousandths of a degree. The current which it is practicable to use is determined not so much by the temperature rise in the resistor, as by the time required to reach a steady state after the battery circuit is closed. If this time is appreciably longer than the period of the galvanometer, observation becomes difficult and tiresome, particularly in the case where balance of the bridge is determined by closing and opening the battery circuit. If the method of battery reversals is used, with a very quick-acting reversing key, larger measuring currents can be used, and the sensitivity is of course twice that of the other method for the same current.

It is customary to assume that, in the range from 0 to 500 °C, the temperature rise produced by a constant measuring current is independent of the temperature. The experiments of F. E. Smith[16] and of Waidner and Burgess[22] indicate that in this range, with constant current, the greater power dissipated in the resistor at the higher temperatures is more readily transferred, presumably by the increased radiation. It is also customary to assume that the temperature rise produced by the measuring current is independent of the medium in which the thermometer is placed.

If the measuring current heats the resistor the same fraction of a degree at all temperatures, the calculated temperatures will be the same as if there had been no heating at all. In cases where there is doubt as to whether the heating is the same at all temperatures or in different media at one temperature, the observed resistances may be corrected to those corresponding to zero measuring current by making observations with two different measuring currents. Some of the newer bridges are so arranged that one pre-selected measuring current is obtained by closing one battery key, and another by closing a second key. The larger current will usually be determined by considerations such as those mentioned earlier in this section. The smaller current should be selected so that the accuracy of the extrapolated value of resistance corresponding to zero current shall be a maximum. Assuming that the temperature rise varies as the square of the current, sensitivity directly as the current, and with the usual assumptions concerning combination of errors, the optimum value of the ratio of the currents can be determined. The author is indebted to Mr. R. B. Scott for the solution, which is that the smaller current should be 0.56 of the larger. Since this is the condition for a maximum it follows that some departure from this ratio will not affect the accuracy appreciably. Accordingly it is permissible to make the ratio 0.5 (corresponding to ¼ the heating effect) or 0.71 (corresponding to ½ the heating effect) if either is considered more convenient than the optimum of 0.56.

6. Errors

In either the Callendar or the Van Dusen formula the measured resistances enter only in the term

$$\frac{R_t - R_0}{R_{100} - R_0} 100$$

which involves the ratio of two differences of resistance. It is obvious that the ratio will be unchanged if a constant of any magnitude whatever is added to or subtracted from each of the resistances in the expression, and also that the value of the ratio will be unaltered if each of the resistances is multiplied by the same factor.

The expression may be written either as

$$\frac{R_t - R_0}{R_{100} - R_0} \cdot 100 \text{ or as } \frac{R_t - R_0}{R_0 C}$$

In using a calibrated thermometer it may be better in some cases to consider $R_{100} - R_0$ as unchanged, and in the other cases to consider C as unchanged, in case the observed value of R_0 differs from that obtained during the calibration, or in case the observed value of R_0 is found to change slightly with use.

The decision will be found to depend upon the reasons for the observed changes in R_0. If the change in R_0 was one which affected all other values of resistance by an equal amount, the value $R_{100} - R_0$ should be considered constant and used in calculations; whereas if the change was one which affected all other values of resistance in the same proportion, the value of C should be considered constant and used in calculations. That this was true in a particular case has been demonstrated at the expense of about two pages of algebra.[28]

These generalizations doubtless are valid for temperatures down to about − 190 °C, the present limit of the International Temperature Scale, but they may be expected to fail for very low temperatures.

Changes in the thermometer alone will be considered first. The most obvious case is that of a thermometer with compensating leads, of either the Siemens or Callendar type. It is obvious that if the resistance of the leads in one arm of the bridge changes relatively to that of the leads in the adjacent arm, the effect will be to increase or decrease all observed resistances by the same amount. The fact that thermometer leads were subject to such changes is doubtless the basis for the rather common practice of considering R_0 a variable, and $R_{100} - R_0$ and δ as the constants of a thermometer.

The modern resistance thermometer, however, is made with current and potential leads, and is immune to changes of the kind mentioned in the preceding paragraph. The resistor of such an instrument may be securely mounted so that it is not subject to mechanical deformations, and is subject to changes resulting primarily from heat treatment. The changes which may result from heat treatment may be caused by contamination, or by strain or relief of strain. All such changes are approximately subject to the Matthiessen rule that the temperature coefficient of the resistance added (or subtracted) by contamination or strain is very low. The changes of resistance which occur in the resistor of the thermometer are therefore likely to be additive.

Changes which affect the resistance of the thermometer at all temperatures in the same proportion are much less likely to occur. They might conceivably result from evaporation of platinum, or from actual lengthening or shortening of the wire, followed by an annealing sufficient to restore the original physical condition. None of these appears as likely to occur as the kind of changes which result in an additive resistance.

Secondly, the changes which may be introduced by the resistance-measuring equipment must also be considered. Taking the Wheatstone bridge as an example, a change in the bridge zero, if not determined and taken into account, would introduce an additive resistance. The bridge zero, however, is so easily determined that such an additive change need not affect results. Another change that may be treated as additive is any change in the resistance of coils which remain in circuit during measurements of both R_t and R_0. It may be that such changes are part of a proportional change, and if this is known to be the case, the change should be treated accordingly.

In the resistance-measuring equipment, proportional changes are introduced by a change in the resistance unit, such as might occur in changing from one bridge to another, where the bridges had been calibrated with different standards or in terms of a "box unit" which might be defined as 0.1, the sum of the resistances of the ten one-ohm coils. A relative change in the ratio arms of a bridge, if not determined and taken into account or eliminated, would be equivalent to a change in the resistance unit. A change in the temperature of the bridge coils, if not determined and taken into account, would in general, produce a proportionate change in all resistances measured, strictly so if all the coils had equal temperature coefficients and were subjected to equal changes in temperature.

In general, if a change in R_0 is observed, this change, if it originates in the thermometer itself, is most likely to be an additive one; but if it originates in the resistance-measuring equipment, it is more likely to be a proportional change. The procedure to be followed in particular cases may be inferred from the foregoing discussion.

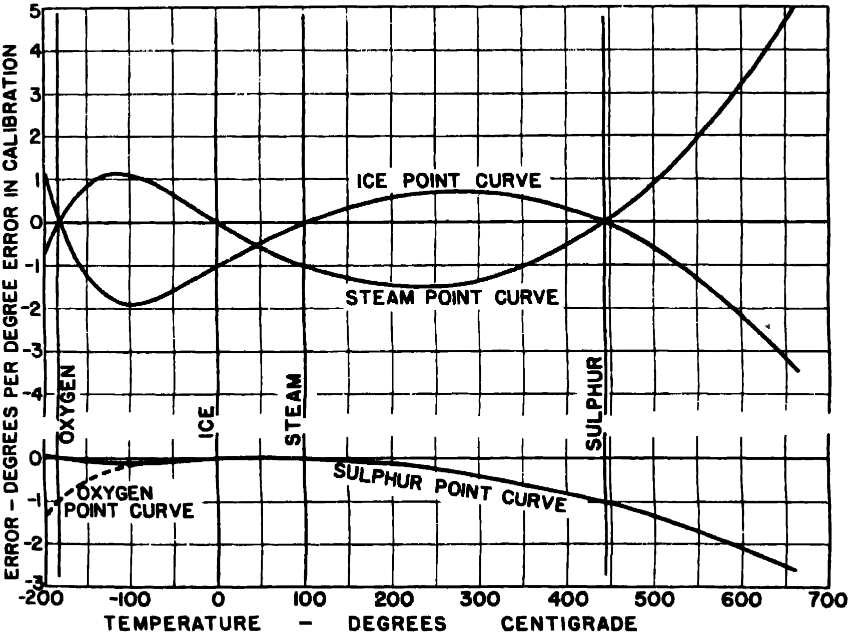

FIG. 2. Effects at various temperatures of errors made in calibrating a platinum resistance thermometer.

(1) If the thermometer is calibrated and used with one bridge only, and if the value of R_0 changes by small amounts, it may be possible to infer whether the observed changes are in the resistor of the thermometer or in the resistance-measuring equipment. In the former case, $R_{100} - R_0$ is treated as constant and in the latter, C is treated as constant. If the change in R_0 is more than two or three

times as large as the permissible error in the result, a redetermination of R_0 and R_{100}, or a recalibration of the bridge, or both, is in order.

(2) If a thermometer is calibrated with one bridge and used with another, the resistance units may be different, and in transferring, the value of C is to be considered constant. The value of R_0 is determined using the second bridge, and the corresponding value of $R_{100} - R_0$ may then be computed. Later changes in R_0 are to be treated as in the first case discussed.

(3) If the measurements are made at temperatures near 0 °C, the current value of R_0 is the best to use, and it makes very little difference whether $R_{100} - R_0$ or C is used as the constant of the thermometer. For example, in measuring a temperature of about 25 °C using a bridge without temperature control, both R_{25} and R_0 should be measured. The error in the temperature determined from these two values will obviously be much smaller than the value which would have been obtained if R_0 had not been determined and used.

H. J. Hoge has derived expressions (unpublished) for the values of the differential coefficients in the expression obtained by differentiating the Van Dusen equation, namely

$$dt = \frac{\partial t}{\partial R_0}dR_0 + \frac{\partial t}{\partial R_{100}}dR_{100} + \frac{\partial t}{\partial R_s}dR_s + \frac{\partial t}{\partial R_{O_2}}dR_{O_2} + \frac{\partial t}{\partial R_t}dR_t$$

By using these coefficients in expressions of the type $\frac{\partial t}{\partial R_0}\left[\frac{dR}{dt}\right]_{t=0}$ he has calculated the factors by which a unit error in temperature, made during calibration, in determining any of the four resistances, R_0, R_{100}, R_s (resistance at 444.6 °C) and R_{O_2} (resistance at −182.97 °C) must be multiplied to find the corresponding error in any calculated temperature. His results are shown graphically in Fig. 2, and in the following table.

Temp. (°C)	Multiplying factors for errors at			
	Ice Point	Steam Point	Sulfur Point	Oxygen Point
−200	+1.0	−0.8	+0.1	−1.4
−183	0.0	0.0	0.0	−1.0
−100	−1.9	+1.1	−0.1	−0.1
0	−1.0	0.0	0.0	0.0
50	−0.5	−0.5	0.0	0.0
100	0.0	−1.0	0.0	0.0
200	+0.6	−1.5	−0.1	0.0
300	+0.7	−1.3	−0.4	0.0
400	+0.3	−0.5	−0.8	0.0
445	0.0	0.0	−1.0	0.0
500	−0.6	+0.9	−1.3	0.0
600	−2.1	+3.2	−2.1	0.0
630	−2.7	+4.3	−2.3	0.0

This table is to be interpreted as follows. The resistance of the thermometer at any one temperature is assumed to be absolutely constant, that is, it is assumed that no change has occurred in the thermometer since it was calibrated, and that the resistance at any temperature is independent of previous history. The errors dR_0, etc. are those made in calibrating, and represent the difference between the value found and the "true" value. It is obvious, with these assumptions, that if the measured temperature is that of any of the calibration points, calibration errors at any of the other points will have no effect, while an error in the calibration at that point equivalent to a unit error in temperature, will have an effect of the same size but of opposite sign on the calculated temperature, that is, the tabular factor is −1.

As an example, if the value of R_{100} obtained in calibration had actually corresponded to a temperature of 100.01 °C and if in a later measurement of temperature, the resistance was found to be equal to R_{100} as given by the calibration, the calculated temperature would be 100.00. Again, if the temperature measured had been near 600 °C and the R_{100} obtained in calibration had corresponded to 100.01 °C, the temperature calculated from the measured R_t would have been 0.032° too high, if there had been no errors in calibration or measurement except the calibration error at the steam point.

While these assumptions may not correspond exactly to the conditions of actual use, they do serve to show in general the effects of errors made in calibration. The data and Fig. 2 also show that errors in calibration at 0 and 100 °C, if of the same sign so that the fundamental interval is correctly determined, neutralize each other to a large extent, except in the range 0 to 100 °C. Since by definition, the constant β is zero for temperatures above 0 °C, errors in calibration at the oxygen point will produce no errors at temperatures above 0 °C.

7. The International Temperature Scale

It is again necessary to give the credit to Callendar for the first suggestion of a temperature scale of the kind which was adopted in 1927 as the International Temperature Scale. His papers on a proposed standard temperature scale[38, 39] anticipate many of the features of the present scale, although his proposals differed in regard to some details. His arguments concerning the need of adopting such a standard scale and the advantages of doing so are substantially those which have been repeated many times since.

The preëminent position of the platinum resistance thermometer as an instrument of precision is shown by the fact that it was selected to define the International Temperature Scale[40] from −190 to +660 °C. The Callendar formula is used from 0 to 660 °C and the Van Dusen formula from 0 to −190 °C. When the scale was adopted, it was apparently considered more dignified to write the equations in the form of power series in t, rather than in the forms in which they are actually used. This had at least one unfortunate consequence.

It was well known that if a thermometer were properly made of pure platinum, the value of $\dfrac{R_{100}}{R_0}$ would be greater than 1.390 and that the value of δ would be less than 1.51. The requirement that R_{100}/R_0 shall be greater than 1.390 is sufficient to define the purity of the platinum. The additional requirement concerning the value of δ is in the nature of a safeguard against defective construction, or against experimental errors in calibration, and is effectively a specification for the completed thermometer rather than for the platinum. The two requirements mentioned were originally acceptable for the specifications for the International Temperature Scale, but unfortunately, when the form of the equations was changed, the equivalent change in the requirements was not made. The requirements in the International Scale are that R_{100}/R_0 be greater than 1.390 and that $R_{444.6}/R_0$ be greater than 2.645. Each of these requirements relates to the value of $\dfrac{\Delta R}{\Delta t}$ over a specified temperature interval, and neither contains any restriction not implied in the other. The limitation on the value of δ is in effect a limitation on the curvature of the graph of resistance against temperature. Since the limitation on δ is a safeguard against experimental error, it is desirable to set upper and lower limits to its value.

If it is desirable not to mention δ in the International Scale, an equivalent requirement is that

$$\frac{R_{444.6} - R_0}{R_{100} - R_0}$$

shall be between 4.216 and 4.218; or the same requirement can be expressed in other ways. For similar reasons the additional requirement for the thermometer to be used at low temperatures, that R_{-183}/R_0 be less than 0.250 might well be replaced by the requirement that

$$\frac{R_0 - R_{-182.97}}{R_{100} - R_0}$$

shall be between 1.925 and 1.928.

These changes should have come up for consideration at the scheduled meeting of the International Conference on Weights and Measures in 1939, but action on them will necessarily be delayed until certain differences of opinion on non-scientific matters shall have been adjusted.

In retrospect, the general review of the development of the subject serves only to emphasize the predominant importance and the completeness of the late Prof. Callendar's work in resistance thermometry. The mere fact that resistance thermometry was, somewhat unjustly, in disfavor when he began, and that he left it in nearly its present state, is in itself a high tribute to the man and his work.

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Thermoelectric Thermometry

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I. Introduction

Study in the field of thermoelectricity began in 1821 with the discovery of Seebeck[1] that an electric current flows continuously in a closed circuit of two dissimilar metals when the junctions of the metals are maintained at different temperatures. In the early investigations of thermoelectric effects the results were expressed more qualitatively (in terms of the direction of the current flowing in a closed circuit) than quantitatively, because the relations between the measurable quantities in an electric circuit were not well known at the time.*

II. Fundamental Laws

As a result of a large number of investigations of thermoelectric circuits in which accurate measurements were made of the electromotive force, current, and resistance, several "established facts" or "laws" have been formulated. These facts or laws, variously stated in different ways and combinations and sometimes consolidated into a general statement of the phenomenon discovered by Seeback, can be reduced to three fundamentals:

(1) the law of the homogeneous circuit;
(2) the law of intermediate metals;
(3) the law of successive or intermediate temperatures.

The latter two may be arrived at by applying the laws of thermodynamics to the thermoelectric circuit, but the fundamental experimental fact regarding a homogeneous circuit, which enters into all measurements of temperature by thermoelectric methods, cannot be derived from such considerations. The law of the homogeneous circuit is incorporated into most statements of the law of intermediate metals. In any case all these facts or laws, as stated below and used in the measurement of temperatures, have been established experimentally beyond a reasonable doubt; and in order that temperatures may be measured by this method the laws must be accepted, in spite of any lack of rigor that may appear in any of the thermodynamic derivations given here or elsewhere.

The discussion will be simplified by defining a few terms at this point. It will be considered that all the metals comprising a thermoelectric circuit are solids unless otherwise stated.

A pair of electrical conductors so joined as to produce a thermal emf when the junctions are at different temperatures is known as a thermocouple. The resultant emf developed by the thermocouples generally used for measuring temperatures ranges from 1 to 7 millivolts when the temperature difference between the junctions is 100 °C.

If in a simple thermoelectric circuit (Fig. 1), the current flows from metal *A* to metal *B* at the colder junction, *A* is generally referred to as thermoelectrically positive to *B*. In determining or expressing the emf of a thermocouple as a function of the temperature, one junction is maintained at some constant reference temperature, such as 0 °C, and the other is at the temperature corresponding to the emf. In the present paper, the order in which the metals are named and the sign of the numerical value of the emf will be used to indicate which of the metals is positive to the other at the junction which is at the reference temperature. For example, if in Fig. 1, T_1 is the reference temperature and the current flows in the direction indicated, the emf of thermocouple *AB* will be positive, and the emf of thermocouple *BA* will be negative.

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* The relation between the current and potential difference in an electric circuit was first clearly stated by G. S. Ohm in 1826. *Schweigger's Journal,* **46,** 137 (1826).

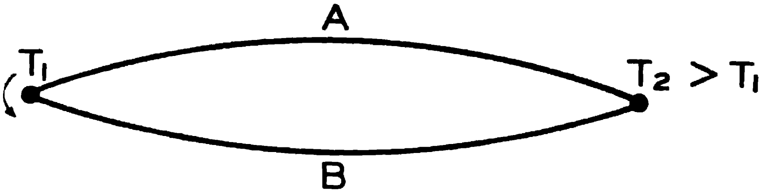

FIG. 1. Simple thermoelectric circuit.

1. **The law of the Homogeneous Circuit.** *An electric current cannot be sustained in a circuit of a single homogeneous metal, however varying in section, by the application of heat alone.* As far as we know this principle has not been derived theoretically. It has been claimed from certain types of experiments that a nonsymmetrical temperature gradient in a homogeneous wire gives rise to a galvanometrically measurable thermoelectric emf. However, the overwhelming weight of evidence indicates that any emf observed in such a circuit is to be attributed to the effects of local inhomogeneities. As a matter of fact, at the present time, any current detected in such a circuit when the wire is heated in any way whatever is taken as evidence that the wire is inhomogeneous. The most important of a large number of investigations of this subject are adequately discussed by Foote and Harrison.[2]

In the present paper, we accept as an experimental fact the general statement that the algebraic sum of the electromotive forces in a circuit of a single homogeneous metal, however varying in section and temperature, is zero. As a consequence of this fact, if one junction of two dissimilar homogeneous metals is maintained at a temperature T_1 and the other junction at a temperature T_2, the thermal emf developed is independent of the temperature gradient and distribution along the wires.

2. **Law of Intermediate Metals.** This law is stated in one of several ways, and although the statements may appear quite different, they are really equivalent, with the exception that the law of the homogeneous circuit is included in some of the statements. One statement of this law is: *The algebraic sum of the thermoelectromotive forces in a circuit composed of any number of dissimilar metals is zero, if all of the circuit is at a uniform temperature.* This law follows as a direct consequence of the second law of thermodynamics, because if the sum of the thermoelectromotive forces in such a circuit were not zero, a current would flow in the circuit. If a current should flow in the circuit, some parts of it would be heated and other parts cooled, which would mean that heat was being transferred from a lower to a higher temperature without the application of external work. Such a process is a contradiction of the second law of thermodynamics, and therefore we conclude that the algebraic sum of the thermoelectromotive forces is zero in such a circuit.

Combining this law with that for a homogeneous circuit, it is seen that in any circuit, if the individual metals between junctions are homogeneous, the sum of the thermal electromotive forces will be zero provided only that the junctions of the metals are all at the same temperature.

Another way of stating the law of intermediate metals is: *If in any circuit of solid conductors the temperature is uniform from any point* P *through all the conducting matter to a point* Q, *the algebraic sum of the thermoelectromotive forces in the entire circuit is totally independent of this intermediate matter, and is the same as if* P *and* Q *were put in contact.* Thus it is seen that a device for measuring the thermoelectromotive force may be introduced into a circuit at any point without altering the resultant emf, provided that the junctions which are added to the circuit by introducing the device are all at the same temperature. It is also obvious that the emf in a thermoelectric circuit is independent of the method employed in forming the junction as long as all of the junction is at a uniform temperature, and the two wires make good electrical contact at the junction, such as is obtained by welding or soldering.

A third way of stating the law of intermediate metals is: *The thermal emf generated by any thermocouple* AB *with its junctions at any two temperatures,* T_1 *and* T_2, *is the algebraic sum of the emf of a thermocouple composed of* A *and any metal* C, *and that of one composed of* C *and* B, *both with their junctions at* T_1 *and* T_2.

$$\text{or, } E_{AB} = E_{AC} + E_{CB}$$

From this statement of the law it is seen that if the thermal emf of each of the metals *A*, *B*, *C*, *D*, etc. against some reference metal is known, then the emf of any combination of these metals can be obtained by taking the algebraic differences of the emfs of each of the metals against the reference metal. Investigators tabulating thermoelectric data have employed various reference metals, such as mercury, lead, copper, and platinum. At present it is customary to use platinum because of its high melting point, stability, reproducibility, and freedom from transformation points.

3. Law of Successive or Intermediate Temperatures. *The thermal emf developed by any thermocouple of homogeneous metals with its junctions at any two temperatures* T_1 *and* T_3 *is the algebraic sum of the emf of the thermocouple with one junction at* T_1 *and the other at any other temperature* T_2 *and the emf of the same thermocouple with its junctions at* T_2 *and* T_3. Considering the thermocouple as a reversible heat engine and applying the laws of thermodynamics to the circuit, it will be shown in the next section that

$$E = \int_{T_1}^{T_3} \phi \, dT$$

from which it follows that

$$E = \int_{T_1}^{T_2} \phi \, dT + \int_{T_2}^{T_3} \phi \, dT$$

This law is frequently invoked in the calibration of thermocouples and in the use of thermocouples for measuring temperatures. It will be discussed in detail in Section IV.

The above are all the fundamental laws required in the measurement of temperatures with thermocouples. They may be, and frequently are, combined and stated as follows: *The algebraic sum of the thermoelectromotive forces generated in any given circuit containing any number of dissimilar homogeneous metals is a function only of the temperatures of the junctions.* It is seen then that if all but one of the junctions of such a given circuit are maintained at some constant reference temperature, the emf developed in the circuit is a function of the temperature of that junction only. Therefore, by the proper calibration of such a device, it may be used to measure temperatures.

It should be pointed out here that none of the fundamental laws of thermoelectric circuits, which make it possible to utilize thermocouples in the measurement of temperatures, depends upon any assumption whatever regarding the mechanism of interconversion of heat and electrical energy, the location of the emfs in the circuit, or the manner in which the emf varies with temperature.

III. Historical Investigation and Theory

Although a knowledge of the location of the electromotive forces in a thermoelectric circuit and of the mechanism by which heat is converted into electrical energy is not required in order to measure temperatures with thermocouples, any information available on these subjects may be used advantageously in studying the characteristics of thermocouples and their behavior during use. Various theoretical and experimental investigations of thermoelectric circuits give us the location of the electromotive forces in such a circuit, and the relation between these electromotive forces, but they have not yielded a satisfactory explanation of the mechanism by which heat is converted into electrical energy or of the manner in which the electromotive force varies with temperature, except empirical relations.

In 1834 Peltier[3] found that when a current is passed across the junction of two dissimilar metals in one direction heat is absorbed and the junction cooled, and that when the current is passed in the opposite direction the junction is heated. Peltier and others observed that for a given current the rate of absorption or liberation of heat at the junction of two dissimilar metals depends upon the thermoelectric power (dE/dt) of the two metals and is independent of the form and dimensions of the metals at the junction. In 1853 Quintus Icilius[4] showed that the rate at which heat is absorbed or generated at a junction of two dissimilar metals is proportional to the current. This heating or cooling effect discovered by Peltier should not be confused with the Joule heating effect which, being proportional to the electrical resistance and to the square of the current, depends upon the dimensions of the conductor and does not change sign when the current is reversed.

Inasmuch as heat is absorbed when a current flows up a potential gradient and heat is generated when the current flows down a potential gradient, the heating or cooling effect at a junction of two dissimilar metals (being proportional to the current) is evidence that the junction is the seat of an electromotive force. If we let P be the rate at which heat (in joules per second or in watts) is generated or absorbed when a current of one ampere flows across a junction, then P is the Peltier coefficient of the junction (in watts per ampere), or more simply the Peltier emf (in volts). The direction and magnitude of this emf depends upon the metals which form the junctions and upon the temperature.

In 1851, W. Thomson[5] (later Lord Kelvin) concluded, from thermodynamic reasoning and from the then known characteristics of thermocouples, that the reversible absorption of heat at the junctions of dissimilar metals was not the only reversible heat effect in a thermoelectric circuit. In brief he reasoned as follows:

(1) Assuming that the Peltier emfs represent the only reversible effects in a simple thermoelectric circuit, the resultant emf, E, in the circuit is given by

$$E = P_2 - P_1 \tag{1}$$

where P_1 is the Peltier emf of the junction which is at temperature T_1, and P_2 is the Peltier emf of the junction which is at temperature T_2.

(2) Neglecting the effect of thermal conduction (an irreversible process) and considering the thermocouple as a reversible heat engine with a source at the temperature T_2 in degrees Kelvin and a sink at the temperature T_1, we have as a consequence of the second law of thermodynamics

$$\frac{P_2}{T_2} - \frac{P_1}{T_1} = 0 \tag{2}$$

$$\frac{P_2 - P_1}{P_1} = \frac{T_2 - T_1}{T_1} \tag{3}$$

which combined with (1) gives

$$E = P_1 {}^{(T_2 - T_1)} \tag{4}$$

It would follow therefore that if one junction were maintained at a constant temperature, T_1, P_1 would be constant, and the emf, E, would be proportional to $(T_2 - T_1)$. It had been definitely shown by a number of investigators that E was not proportional to $(T_2 - T_1)$. Thomson therefore concluded that the Peltier effects were not the only reversible heat effects in such a circuit and that there must be a reversible absorption of heat due to the flow of current through that part of the conductors in which there is a temperature gradient.

In 1854 Thomson[6] succeeded in showing experimentally that in certain homogeneous metals heat is absorbed when an electric current flows from colder to hotter parts of the metal, and heat is generated when the current flows from the hotter to colder parts. In certain other metals the opposite of this effect occurs, that is, heat is absorbed when an electric current flows from the hotter to the colder parts, and in still other metals, the effect is too small to be detected by the methods used. This heating or cooling effect, called the Thomson effect, being reversible and occurring only where there is a temperature gradient in a metal, is entirely distinct from the irreversible Joule heating.

The reversible absorption of heat in a homogeneous conductor has the same effect as if an electromotive force existed in the temperature gradient. The direction and magnitude of this emf between any two points depend upon the metal, the temperature, and the temperature difference between the two points. If in any metal we let σ equal the rate at which heat is absorbed or generated per unit difference of temperature when a current of one ampere flows; then the total emf between any two points at temperatures T_1 and T_2 is given by

$$\int_{T_1}^{T_2} \sigma \, dT.$$

In a simple thermoelectric circuit of two metals, A and B (Fig. 2), there exist four separate and distinct electromotive forces: the Peltier emfs at the two junctions and the Thomson emfs along that part of each wire which lies in the temperature gradient. The only emf that can be measured as such in this circuit is the resultant emf. The identity of the individual emfs can only be established by observations of the reversible heat effects. The Thomson emf will be considered positive if heat is generated when the current flows from the hotter to the colder parts of the conductor, and negative if the reverse occurs.

Thomson took into consideration the reversible heat effects in the temperature gradient of the conductors (Thomson effects) as well as those at the junctions (Peltier effects), and applied the laws of thermodynamics to the thermoelectric circuit. A complete discussion of this application, together with the hypothesis involved, is given in the original paper by Thomson.[7]

Consider a simple thermoelectric circuit of two metals, A and B (Fig. 2), and let P and $P + \Delta P$ be the Peltier emfs of the junctions at temperature T and $T + \Delta T$ in degrees Kelvin, respectively, and let σ_A and σ_B be the Thomson emfs per degree along conductors A and B respectively. Let the metals and temperatures be such that the emfs are in the directions indicated by the arrows. The resultant emf, ΔE, in the circuit is given by

$$\Delta E = P + \Delta P - P + \sigma_A \Delta T - \sigma_B \Delta T \qquad (5)$$

$$\Delta E = \Delta P + (\sigma_A - \sigma_B)\Delta T \qquad (6)$$

in the limit

$$\frac{dP}{dT} + (\sigma_A - \sigma_B) \qquad (7)$$

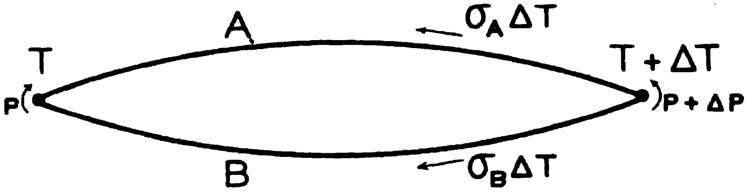

FIG. 2. Location of the electromotive forces in a thermoelectric circuit.

By the second law of thermodynamics $\Sigma\frac{Q}{T}=0$, for a reversible process. If then we regard the thermocouple as a reversible heat engine and pass a unit charge of electricity, q, around the circuit, we obtain by considering only the reversible effects*

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* The following quotations are from the paper by W. Thomson.

"...... The following proposition is therefore assumed as a fundamental hypothesis in the Theory at present laid before the Royal Society.

"The electro-motive forces produced by inequalities of temperature in a circuit of different metals, and the thermal effects of electric currents circulating in it, are subject to the laws which would follow from the general principles of the dynamical theory of heat if there were no conduction of heat from one part of the circuit to another.

"In adopting this hypothesis, it must be distinctly understood that it is only a hypothesis, and that, however probable it may appear, experimental evidence in the special phenomena of thermo-electricity is quite necessary to prove it. Not only are the conditions prescribed in the second Law of the Dynamical Theory not completely fulfilled, but the part of the agency which does fulfill them is in all known circumstances of thermo-electric currents excessively small in proportion to the agency inseparably accompanying it and essentially violating those conditions. Thus, if the current be of the full strength which the thermal electromotor alone can sustain against the resistance in the circuit, the whole mechanical energy of the thermo-electric action is at once spent in generating heat in the conductor;—an essentially irreversible process. The whole thermal agency immediately concerned in the current, even in this case when the current is at the strongest, is (from all we know of the magnitude of the thermo-electric force and absorptions and evolutions of heat) probably very small in comparison with the transference of heat from hot to cold by ordinary conduction through the metal of the circuit.

It is true, we may, as has been shown above, diminish without limit the waste of energy by frictional generation of heat in the circuit, by using an engine to do work and react against the thermal electromotive force; but, as we have also seen, this can only be done by keeping the strength of the current very small compared with what it would be if allowed to waste all the energy of the electromotive force on the frictional generation of heat; and it therefore requires a very slow use of the thermo-electric action. At the

$$\frac{q(P + \Delta P)}{T + \Delta T} - \frac{qP}{T} + \frac{q\sigma_A \Delta T}{T + \frac{\Delta T}{2}} - \frac{q\sigma_B \Delta T}{T + \frac{\Delta T}{2}} \tag{8}$$

which may be written

$$\left(\frac{P}{T}\right) + \frac{(\sigma_A - \sigma_B)\Delta T}{T + \Delta T} = 0 \tag{9}$$

or in the limit

$$\frac{d}{dT}\left(\frac{P}{T}\right) + \frac{1}{T}(\sigma_A - \sigma_B) = 0 \tag{10}$$

or

$$\sigma_A - \sigma_B = \frac{P}{T} - \frac{dP}{dT} \tag{11}$$

Eliminating $(\sigma_A - \sigma_B)$ between (7) and (11)
we have

$$P = T\frac{dE}{dT} \tag{12}$$

Substituting (12) in (10)
we have

$$(\sigma_A - \sigma_B) = T\frac{d^2E}{dT^2} \tag{13}$$

From (12) it is seen that

$$E = \int_{T'}^{T} \frac{P}{T}\,dT = \int_{T'}^{T} \phi\,dT \tag{14}$$

which is the expression referred to earlier.

The Peltier emf at the junction of any two dissimilar metals at any temperature can be calculated from Equation (12) and measurements of the variation of the thermal emf with temperature. The magnitude of the emf existing at the junction of two dissimilar metals ranges from 0 to about 0.1 volt for the metals generally used in temperature measurements.

Although the thermoelectric theory as developed above does not enable us to determine directly the magnitude of the Thomson coefficient in any individual metal, the difference between the Thomson coefficients in two metals can be calculated from Equation (13) and measurements of the variation in thermal emf with temperature. Various types of experiments indicate that the Thomson effect in lead is extremely small, if not zero, at ordinary atmospheric temperatures. Consequently some information regarding the magnitude of the Thomson coefficients in other metals at these temperatures can be determined if it is assumed that this coefficient is zero for lead. On this basis it is found that the Thomson coefficient at 0 °C in microvolts per °C is −9 for platinum, −8 for iron, +2 for copper, −23 for constantan,* −8 for alumel,* −2 for 90 platinum−10 rhodium,* and +9 for chromel P.*

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same time, it does not in any degree restrain the dissipation of energy by conduction, which is always going on, and which will therefore bear an even much greater proportion to the thermal agency electrically spent than in the case in which the latter was supposed to be unrestrained by the operation of the engine. By far the greater part of the heat taken in at all, then, in any thermo-electric arrangement, is essentially dissipated, and there would be no violation of the great natural law expressed in Carnot's principle, if the small part of the whole action, which is reversible, gave a different, even an enormously different, and either a greater or a less, proportion of heat converted into work to heat taken in, than that law requires in all completely reversible processes."

* Alloys used in the measurement of temperatures.

In order to justify the assumption involved in the application of the second law of thermodynamics, it is necessary and sufficient to verify experimentally the relation

$$P = T\frac{dE}{dT} \tag{12}$$

$$\sigma_A - \sigma_B = T\frac{d^2E}{dT^2} \tag{13}$$

Inasmuch as the individual emfs cannot be measured as such, we must depend upon calorimetric measurements of the heating and cooling effects. In order to measure these small reversible effects, it is necessary to separate them from the much larger irreversible Joule heating and the thermal conduction which take place in any experiment of this nature. Practically all the experimental work on this subject has been on the relation given by Equation (12), because the reversible heating effects involved in it are in general much larger and more localized than those in Equation (13).

The most carefully conducted experiments, particularly those of Edlund,[8] Jahn,[9] Caswell,[10] and Borelius[11] indicate that the foregoing relations hold within the accuracy of the measurements, about 5 to 10 per cent. As far as we know, there is no evidence available which would indicate that these relations are not exact.

We cannot integrate Equation (12) or (13) and obtain a general relation between E and T, without some information on the manner in which P or σ varies with T. Experiments indicate that P and σ both depend upon T, but the manner in which they vary with T has not been established, either theoretically or experimentally, with any degree of accuracy.

A number of hypotheses have been made as to the manner in which σ varies with the temperature and Equation (13) then integrated, but in each case it has been found that the type of equation so obtained represents the experimentally determined values of E and T only over limited temperature ranges. Consequently, the relation between E and T for any pair of metals must be determined experimentally, and corresponding values given by tables or empirical relations for limited temperature ranges.

Later theories of thermoelectricity may be divided into two general classes: (1) those in which attempts are made to avoid the hypothesis made by Thomson, and (2) those in which the theory as developed by Thomson is accepted as far as it goes, and attempts are made to derive a reversible mechanism or process for converting heat into electrical energy by the application of the electron theories of metals. The theories in the first general class have added little, if anything, to our knowledge of thermoelectricity. The assumptions involved in most of these appear more objectionable than the one made by Thomson. The relations derived between the quantities involved are either equivalent to or less useful than those derived by Thomson.

The existence of the Peltier and Thomson emfs in a thermoelectric circuit may be deduced, qualitatively at least, from the electron theories of metals, but the uncertainties in the quantities involved are so large that we cannot determine whether or not the theories are in agreement with experimental data. The most that can be claimed for the more complete of these theories at the present time is that they give the order of magnitude of the various effects for certain metals.

IV. Thermoelectric Thermometers

A thermoelectric thermometer is a device for measuring temperatures by utilizing the thermoelectric effects. In its simplest form, it consists of a thermocouple of

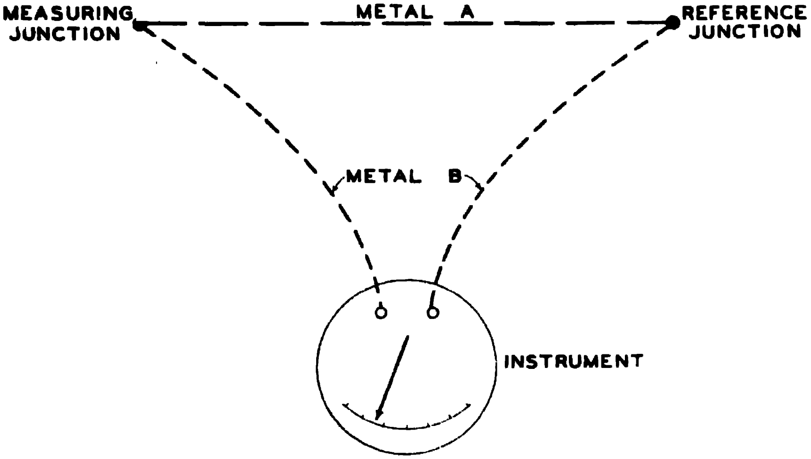

FIG. 3. Simple thermoelectric thermometer.

two dissimilar metals which develop an emf when the junctions are at different temperatures, and an instrument for measuring the emf developed by the thermocouple, connected together as shown in Fig. 3.

As long as the instrument is at essentially a uniform temperature, all the junctions in the instrument, including the terminals, will be at the same temperature; and the resultant thermal emf developed in the circuit is not modified by including the instrument. If the reference junction is maintained at some reference temperature, such as 0 °C, the emf developed by the thermocouple can be determined as a function of the temperature of the measuring junction. The device can then be

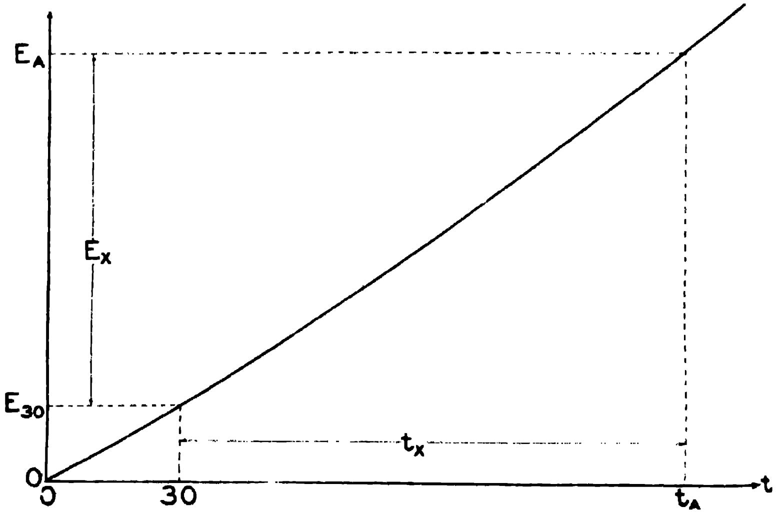

FIG. 4. Illustrating how corrections may be applied for variations in the temperature of the reference junction.

used for measuring temperatures. It is not necessary to maintain the reference junction at the same temperature during use as during calibration. However, the temperature of the reference junction in each case must be known. For example, let the curve in Fig. 4 be the relation between the emf, E, and temperature, t, for a particular thermocouple with the reference junction at 0 °C. Suppose the device is used to measure some temperature, and an emf, E_x, is observed when the reference junction is at 30 °C. We may add the observed emf, E_x, to E_{30} (the emf given by the thermocouple when one junction is at 0 and the other at 30 °C) and obtain from the curve the true temperature, t_A, of the measuring junction. Certain types of instruments which are used with thermocouples in the manner shown in Fig. 3 are such that they can be adjusted manually for changes in the reference junction temperature, and the emf, E_A, can be read directly on the instrument.

Inasmuch as the curves giving the relation between emf and temperature are not, in general, straight lines, equal increments of temperature do not correspond to equal increments of emf.

In many cases the thermocouple is connected to the instrument by means of copper leads as shown in Fig. 5.

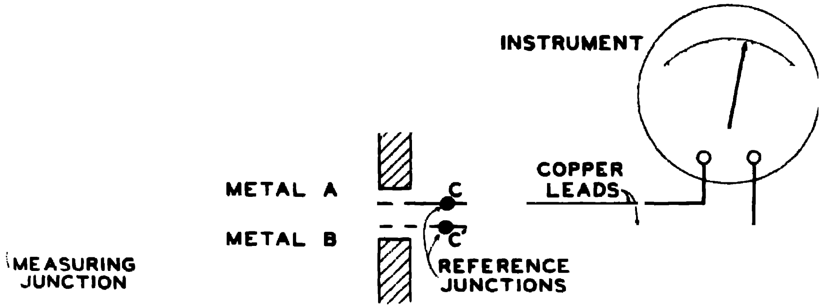

FIG. 5. Diagram for thermoelectric thermometer with copper leads for connecting thermocouple to instrument.

If the junctions C and C' are maintained at the same temperature, which is usually the case, the circuit shown in Fig. 5 is equivalent to that shown in Fig. 3. If the junctions C and C' are not maintained at the same temperature, the resultant thermal emf in the circuit will depend not only upon the thermocouple materials and the temperature of the measuring junction but also upon the temperatures of these junctions and the thermoelectric properties of copper against each of the individual wires. Such a condition should be, and usually is, avoided.

Circuits such as those shown in Figs. 3 and 5 are used extensively in laboratory work where it is usually convenient to maintain the reference junctions, either at 0 °C by placing them in a Thermos bottle filled with cracked or shaved ice and distilled water, or at some other conveniently controlled temperature.

In most commercial installations where it is not convenient to maintain the reference junctions at some constant temperature, each thermocouple wire is connected to the instrument with a lead of essentially the same chemical composition and thermoelectric characteristics as the thermocouple wire, in the manner shown in Fig. 6. This is equivalent to using a thermocouple with the reference junctions at the instrument terminals. Leads which have the same thermoelectric characteristics as the thermocouple wires are called extension leads. In most installations of this nature the instrument is equipped with an automatic reference junction compensator which automatically changes the indication of the instrument to compensate for changes in the temperature of the reference junctions, thus eliminating the necessity of measuring or controlling the reference junction temperature. Such automatic devices are usually part of the instrument, and in such cases the reference junctions should be located in or at the instrument or at some point which is at the same temperature as the instrument.

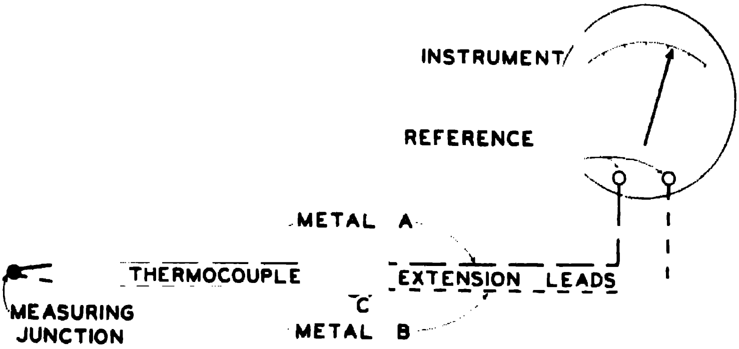

FIG. 6. Thermoelectric thermometer with extension leads.

In some cases where expensive thermocouple wires are used, extension lead wires of less expensive materials are available which give practically the same temperature-emf relation as the thermocouple over a limited temperature range, usually 0 to 100 °C. Although the combined leads give practically the same temperature-emf relation as the thermocouple wires, the individual lead wires are not identical thermoelectrically with the thermocouple wires to which they are attached, and therefore the two junctions where the leads are attached to the thermocouples (*C* and *C′* in Fig. 6) should be kept at the same temperature. This is not necessary in the case of thermocouples where each lead and thermocouple wire to which it is attached are of the same material.

V. Types of Thermocouples

Although a thermal emf is developed when the junctions of any two dissimilar metals are maintained at different temperatures, only certain combinations of metals have been found suitable for use as thermocouples in the measurement of temperatures. Obviously these thermocouples must be such that:

(1) The thermal emf increases continuously with increasing temperature over the temperature range in which the thermocouple is to be used.

(2) The thermal emf is great enough to be measured with reasonable accuracy.

(3) Their thermoelectric characteristics are not appreciably altered during calibration and use either by internal changes, such as recrystallization, or by contamination from action of surrounding materials.

(4) They are resistant to any action such as oxidation, corrosion, etc. which destroys the wire.

(5) The melting points of the metals used must be above any temperature at which the thermocouple is to be used.

(6) The metals are reproducible and readily obtainable in uniform quality.

The combinations of metals and alloys extensively used as thermocouples for the measurement of temperatures in this country are listed in Table 1, together with the temperature ranges in which they are generally used and the maximum temperature at which they can be used for short periods. The period of usefulness of a thermocouple depends upon such factors as the temperature, diameter of wires, accuracy required, conditions under which it is used, etc.

Table 1. Types of Thermocouples and Temperature Ranges in Which They Are Used.

Type of Thermocouple	Usual Temperature Range (°C)	Usual Temperature Range (°F)	Maximum Temperatures (°C)	Maximum Temperatures (°F)
Platinum to Platinum-Rhodium	0 to 1450	0 to 2650	1700	3100
Chromel P to Alumel	- 200 to 1200	- 300 to 2200	1350	2450
Iron to Constantan	- 200 to 750	- 300 to 1400	1000	1800
Copper to Constantan	- 200 to 350	- 300 to 650	600	1100

There are two types* of platinum to platinum-rhodium thermocouples used in this country, the platinum to 90 platinum-10 rhodium and the platinum to 87 platinum-13 rhodium. These thermocouples develop, at high temperatures, 10 to 14 microvolts per °C as compared to 40 to 55 for the other thermocouples listed in Table 1. The platinum to platinum-rhodium thermocouples at temperatures from about 400 to 1600 °C, being more stable than any other combination of metals, are used (1) for defining the International Temperature Scale from 660 °C to the freezing point of gold, 1063 °C, (only the platinum to 90 platinum-10 rhodium thermocouple is used for this purpose); (2) for very accurate temperature measurements from 400 to 1500 °C; and (3) for temperature measurements where the lower melting point materials cannot be used. They are not suitable for temperature measurements below 0 °C because the thermoelectric power $\left(\frac{dE}{dT}\right)$ is only about 5 microvolts per °C at 0 °C and decreases to zero at about −138 °C.

The nominal composition of the chromel P alloy is 90 per cent nickel and 10 per cent chromium. Alumel contains approximately 95 per cent nickel, with aluminum, silicon, and manganese making up the other 5 per cent. Chromel P-alumel thermocouples, being more resistant to oxidation than the other base metal thermocouples listed in Table 1, are generally more satisfactory than the other base-metal thermocouples for temperature measurements from about 650 to 1200 °C (1200 to 2200 °F). The life of a No. 8 gage (0.128″) chromel P-alumel thermocouple is about 1000 hours in air at about 1150 °C (2100 °F).

Constantan was originally the name applied to copper-nickel alloys with a very small temperature coefficient of resistance, but it now has become a general name which covers a group of alloys containing 60 to 45 per cent of copper and 40 to 55 per cent of nickel (with or without small percentages of manganese, iron, and carbon) because all the alloys in this range of composition have a more or less negligible temperature coefficient of resistance. Constantan thus includes the alloys made in this country under such trade names as Advance (Ideal), Copel, Copnic, Cupron, etc., most of which contain approximately 55 per cent of copper and 45 per cent of nickel.

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* Neither of these thermocouples has any distinct advantage over the other. For several years prior to 1922, there were two classes of supposedly platinum to 90 platinum-10 rhodium thermocouples available which differed in thermoelectric properties by about 10 per cent. It was found that one of these contained a large percentage of impurities and that the removal of these impurities eliminated one class of platinum to 90 platinum-10 rhodium thermocouples. However, the scales of a large number of instruments had been graduated to read temperatures directly with these impure thermocouples, and in order to provide thermocouples which would give approximately correct readings with these instruments, the manufacturers supplied platinum to 87 platinum-13 rhodium thermocouples, which were found to give roughly the same temperature-emf relation as the "impure 10% rhodium thermocouple." New instruments were graduated to read temperatures directly with these new thermocouples and consequently more thermocouples were required. This has gone on and now this type of thermocouple is considered unavoidable.

Iron-constantan thermocouples give a slightly higher emf than the other base metal thermocouples in Table 1. They are extensively used at temperatures below about 760 °C (1400 °F). The life of a No. 8 gage iron-constantan thermocouple is about 1000 hours in air at about 760 °C (1400 °F).

Copper-constantan thermocouples are generally used for accurate temperature measurements below about 350 °C (660 °F). They are not suitable for much higher temperatures in air because of the oxidation of the copper.

Combinations of metals other than those listed in Table 1 are sometimes used for special purposes. As examples, at temperatures above −200 °C (−300 °F) chromel P-constantan gives a thermal emf per degree somewhat greater than that of any of the thermocouples listed in Table 1 and is sometimes used when the greater emf is required. Graphite to silicon carbide has been recommended[12] for temperatures up to 1800 °C (3300 °F) and for certain applications in steel plants.

VI. Reproducibility of Thermocouples

One of the first requirements of thermoelectric pyrometers for general industrial use is that the scales of the instruments shall be graduated to read temperature directly. Although the indications of the measuring instruments used with thermocouples depend upon the resultant emf developed in the circuit, the scale of the instrument can be graduated in degrees of temperature by incorporating a definite temperature-emf relation into the graduation of the scale. The temperature can then be read directly if the temperature-emf relation of the thermocouple is identical with that incorporated in the scale of the instrument.

All the thermocouples which have the same nominal composition do not give identical relations between emf and temperature. As a matter of fact, in most cases, two samples of metal which are identical as far as can be determined by chemical methods, are not identical thermoelectrically. This is due in part to the fact that the thermoelectric properties of a metal depend to some extent upon the physical condition of the metal.

It is not practicable to calibrate the scale of an instrument in accordance with the temperature-emf relation of a particular thermocouple and to change the scale each time the thermocouple is replaced. Consequently the scales of such instruments are calibrated in accordance with a particular temperature-emf relation which is considered representative of the type of thermocouple, and new thermocouples are purchased or selected to approximate the particular temperature-emf relation.

If the temperature-emf relations of various thermocouples of the same type are not very nearly the same, corrections must be applied to the readings of the indicator, and the corrections will be different for each thermocouple. When several thermocouples are operated with one indicator, and when thermocouples are frequently renewed, the application of these corrections becomes very troublesome. For extreme accuracy it is always necessary to apply such corrections, but for most industrial processes, thermocouples can be manufactured or selected with temperature-emf relations which are so nearly the same that the corrections become negligible.

The accuracy with which the various types of thermocouple materials can be selected and matched to give a particular temperature-emf relation depends upon the materials and the degree to which the temperature-emf relation is characteristic of the materials available. The differences in the temperature-emf relations of the new platinum to platinum-rhodium thermocouples available in this country rarely exceed 4 to 5 °C at temperatures up to 1200 °C. Consequently, there is no difficulty in selecting a relation between emf and temperature which is adequately characteristic of these thermocouples. The temperature-emf relations used in this country for platinum to platinum-rhodium thermocouples are such that new thermocouples which yield these relations within 2 or 3 °C up to 1200 °C are readily available.

The differences in the temperature-emf relations of base-metal thermocouples of any one type are so large that the selection of a temperature-emf relation which might be considered characteristic of the type of thermocouple is difficult and more or less arbitrary. The relations generally used for some of these thermocouples by some manufacturers have been changed from time to time because of differences introduced in the thermoelectric properties of the materials by variations in raw materials and methods of manufacture. However, the relations in use at the present time are such that materials can generally be selected and matched to yield the adopted relations with an accuracy of about ±3 °C up to 400 °C and to ±¾ per cent at higher temperatures. In special cases, materials may be selected to yield the adopted relations within 2 or 3 °C for limited temperature ranges.

VII. Temperature-Emf Relations

Corresponding values of temperature and emf which are considered characteristic of the various types of thermocouples are given in Table 2. More detailed tables will be found in the references given in the table. As far as we know, the corresponding values given for platinum to 90 platinum-10 rhodium, platinum to 87 platinum-13 rhodium, and chromel P-alumel thermocouples are more or less standard and are the only ones used in this country for these types of thermocouples. The temperature-emf relation of chromel P-alumel thermocouples has been fairly well controlled because these materials are manufactured primarily with controlled thermoelectric properties for thermocouples by only one company.

The values for iron-constantan headed "A" were determined at the National Bureau of Standards a few years ago as being characteristic of the iron and Constantan generally available at that time. The values for iron-constantan headed "B" have been used by certain pyrometer manufacturers for a number of years and presumably are characteristic of the materials available at the time the corresponding values were determined. Owing to the differences in the thermoelectric properties of different lots of iron and constantan, materials must be selected and properly matched in order to obtain a thermocouple which will approximate a selected temperature-emf relation for this type of thermocouple.

Until recent years copper-constantan thermocouples were used primarily for accurate measurements at temperatures below about 350 °C, and in such cases it is customary to calibrate each thermocouple or lot of wire and use an instrument calibrated in millivolts. However, in recent years, there has been an increasing demand for direct reading instruments for use with copper-constantan thermocouples. There are large differences in the temperature-emf relations of copper-constantan thermocouples and consequently the materials must be selected in order to obtain thermocouples which will yield any specified temperature-emf relation. No difficulty has been encountered in obtaining thermocouples which will give very closely the temperature-emf relation in Table 2.

Table 2. Corresponding Values of Temperature and Emf for Various Types of Thermocouples.

Temp. (°C)	90 Pt-10 Rh to Platinum[1] (mv)	87 Pt-13 Rh to Platinum[1] (mv)	Chromel P to Alumel[2] (mv)	Iron to Constantan		Copper to Constantan[5] (mv)
				A[3] (mv)	B[4] (mv)	
−200			−5.75	−8.27		−5.539
−100			−3.49	−4.82		−3.349
0	0.000	0.000	0.00	0.00	0.00	0.000
+100	0.643	0.646	+4.10	+5.40	+5.28	+4.276
200	1.436	1.464	8.13	10.99	10.78	9.285
300	2.315	2.394	12.21	16.56	16.30	14.859
400	3.250	3.398	16.39	22.07	21.82	20.865
500	4.219	4.454	20.64	27.58	27.39	
600	5.222	5.561	24.90	33.27	33.16	
700	6.260	6.720	29.14	39.30	39.19	
800	7.330	7.927	33.31	45.72	45.48	
900	8.434	9.177	37.36	52.29	51.82	
1000	9.569	10.470	41.31	58.22	58.16	
1100	10.736	11.811	45.14		64.50	
1200	11.924	13.181	48.85			
1300	13.120	14.562	52.41			
1400	14.312	15.940	55.81			
1500	15.498	17.316				
1600	16.674	18.679				
1700	17.841	20.032				

[1] *Bur. Standards J. Research* **10,** 275 (1933) R.P. 530

[2] *J. Research Nat. Bur. Standards* **14,** 239 (1935) R. P. 767

[3] *J. Research Nat. Bur. Standards* **20,** 337 (1938) R. P. 1080.

[4] Catalogs. Leeds & Northrup Co. and Brown Instrument Co.

[5] "Pyrometry," p. 165 (Symposium published by Am. Inst. Mining Met. Engrs., 1920). Int. Crit. Tables Vol. **1**, p. 58, 1926. *J. Research Nat. Bur. Standards* **20,** 337 (1938) R. P. 1080.

VIII. Instruments

Instruments used to measure the emf developed by thermocouples or to indicate the temperature of the measuring junction of a thermocouple may be divided into two general classes: (1) Those operating upon the galvanometric principle, such as ordinary millivoltmeters; and (2) those operating upon the potentiometric principle. At one time there was considerable interest in a class of instruments which operate upon a combination of the galvanometric and potentiometric principles, but at the present time there appears to be no place or demand for such instruments.

Millivoltmeters. A millivoltmeter consists of a coil of wire suspended between the poles of a permanent magnet so that the coil is free to move. A pointer is attached to the coil and moves over a scale graduated in millivolts or in degrees. Leads from the thermocouple are connected to the terminals of the coil, usually through a series resistance, and the emf generated in the thermocouple circuit sends a current through the coil, causing it to deflect in the magnetic field. The magnitude of the deflection depends upon the current through the coil, which in turn depends on the emf generated by the thermocouple and the resistance of the circuit. The current, I, in the circuit is given by

$$I = \frac{E}{R_g + R_x}$$

where E is the resultant emf in the circuit, R_g the resistance of the millivoltmeter, and R_x the resistance of the thermocouple and leads. The potential difference, E_g, across the terminals of the instrument is given by

$$E_g = \frac{R_g}{R_g + R_x} E$$

Millivoltmeters are ordinarily calibrated to indicate *E* correctly when connected to a thermocouple and leads of combined resistance R_x. Any change then in either R_g or R_x causes a change in the indications of the instrument. Inasmuch as instruments are frequently used with more than one thermocouple, and inasmuch as R_x varies with the temperature and the amount of the wire heated, it is desirable to make R_g large compared to R_x or at least to variations in R_x. However, this cannot be accomplished in most instances because the design of a millivoltmeter for any particular service is a compromise between sensitivity and ruggedness, which to a large extent determines the resistance. Millivoltmeters with a resistance of much over 600 ohms become extremely delicate and cannot be used in many locations. In order to obtain the ruggedness required it is necessary in some instances to make R_g as low as 12 or 15 ohms. This means that variations in the resistance of the circuit have an appreciable effect upon the indications of the instrument. Because of these inherent sources of error, millivoltmeters are not very extensively used at the present time.

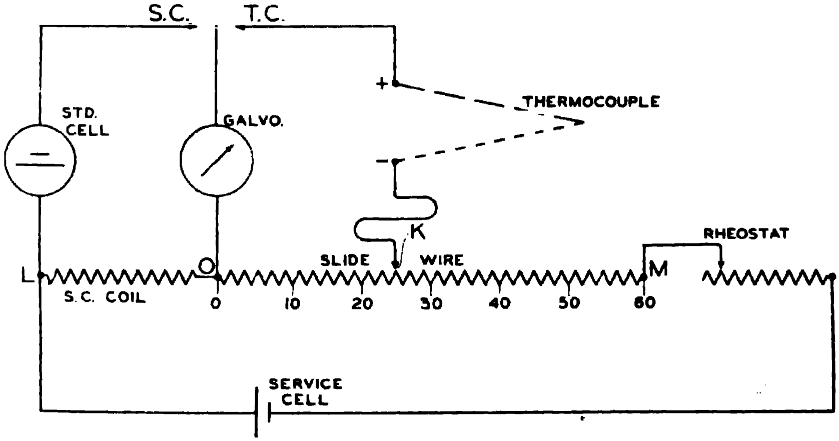

FIG. 7. Diagram of a potentiometer circuit

Potentiometers. The fundamental principle of the potentiometer may be seen by referring to Fig. 7. The current from a service cell, which may be a dry cell or a storage cell, passes through the main circuit composed of a series of fixed resistors, and can be adjusted by a variable rheostat. The relative values of the fixed resistors and the magnitude of the current determine the range of the instrument. By means of a switch either the standard cell or the thermocouple can be connected to the main circuit and its voltage balanced, through a galvanometer, against an equal voltage drop developed in a portion of the main circuit. The potential drop across the various fixed resistors is made to correspond to definite and reproducible values of voltage by adjusting the current to some standard value.

To standardize the battery current, the switch S. C. is closed and the current adjusted until the potential drop across the resistor *LO* is equal to the emf of the standard cell. The emf of the thermocouple can then be determined by closing the T. C. switch and moving the contact *K* until the potential drop in the resistors in the main circuit from *O* to *K* is equal to the emf of the thermocouple. The potential drop from *O* to *K* is read on some suitable scale. The resistors included between *O* and *M* may be made up of fixed coils, a slidewire, or a combination of the two.

The galvanometer has no measuring function but serves solely to indicate zero current in its branch of the circuit. As there is no current through the galvanometer and thermocouple when a balance is obtained, the reading of the potentiometer is independent of the resistance of the thermocouple circuit. However, large changes in this resistance affect the precision of balancing, because as the resistance is increased the sensitivity of response of the galvanometer is decreased, and the greater is the change in emf required to produce a perceptible deflection of the galvanometer. It is therefore advisable to keep the resistance of the thermocouple and leads within reasonable limits as determined by the characteristics of the galvanometer.

There are several important advantages in the potentiometer method. The scale is easily made very open, thus permitting precise readings if a suitable galvanometer is used. The accuracy of the potentiometer is in no way dependent upon the constancy of magnets, springs, or jewel bearings, nor upon the level of the instrument. Insofar as temperature measurements with thermocouples are concerned, the greatest advantages are the accuracy and the complete elimination of any error due to ordinary changes in the resistance of the thermocouple and leads. The objections to the potentiometer are its higher initial cost and the fact that, except for automatic instruments, a manual adjustment must be made to obtain a reading. In the recording and controlling potentiometer equipment, however, all the various manipulations may be performed automatically, even to standardizing the battery current.

Potentiometers are used for practically all laboratory work where the highest accuracy is required. At the present time the large part of the instruments in industrial use operate upon the potentiometric principle.

The scales of millivoltmeters or potentiometers may be calibrated either in millivolts or in degrees of temperature for a particular type of thermocouple. Either type of instrument can be made automatically recording and can be equipped with devices for automatically controlling the temperature of a process or furnace.

Inasmuch as the emf developed by a thermocouple depends upon the temperature of the reference junctions as well as upon the temperature of the measuring junction, corrections must be made for changes in the reference junction temperature unless they are automatically taken care of by the instrument. If properly calibrated, an ordinary millivoltmeter will indicate the temperature of the measuring junction when the pointer of the indicator is set to read the reference junction temperature on open circuit. If the reference junction temperature is well controlled, this adjustment may be made conveniently by hand. However, if this junction is subject to frequent temperature changes, it is advisable to locate the reference junctions at the instrument and use an instrument which automatically changes the indication to compensate for changes in the reference junction temperature. In the case of millivoltmeters this is accomplished automatically by attaching a properly adjusted bimetallic spring to the control spring of the moving coil. If an instrument is equipped with an automatic reference junction compensator for one type of thermocouple, it should not be used with other types nor should it be used in any case unless the reference junctions are located at the instrument.

Potentiometers for industrial use are usually provided with either a hand-operated or an automatic reference-junction compensator. A hand-operated compensator is an adjustable resistor, having a scale graduated in millivolts, which the operator sets to correspond to the observed reference-junction temperature. This operation is equivalent to moving the fixed end of the thermocouple circuit (point *O*, Fig. 7) to a point corresponding to reference-junction temperature. For use with any one type of thermocouple the compensator may include a nickel coil which varies in resistance as the temperature changes and thus compensates automatically for changes in the reference-junction temperature. An instrument so equipped is usually calibrated directly in degrees of temperature. Although it is usually at the instrument, an automatic compensator can be located wherever desired. Lead wires from thermocouple to the compensator location in any case must have the same thermoelectric characteristics as the thermocouple wires.

Instruments calibrated in millivolts are generally used:

(1) when very accurate temperature measurements are to be made with individually calibrated thermocouples;

(2) when used with various types of thermocouples.

Instruments are generally calibrated in degrees of temperature:

(1) when used in industrial plants with only one type of thermocouple;

(2) when the inconvenience of converting millivolt values to temperature is considered more important than the errors introduced by the lack of reproducibility of thermocouples of any one type.

Instruments are ordinarily equipped with manually operated reference junction compensators:

(1) when used with various types of thermocouples;

(2) when the reference junctions are not located at the instrument.

Instruments are ordinarily equipped with automatic reference junction compensators:

(1) when the reference junctions are located at the instrument and subject to considerable variations in temperature;

(2) when the inconvenience of making manual adjustments or arithmetical corrections is considered more important than the errors introduced by using automatic compensators.

IX. Protection Tubes

One of the reasons why the materials listed in Table 1 have come into common use for thermocouples is that they are reasonably stable thermoelectrically when heated in a clean oxidizing atmosphere. The standards of performance which are generally accepted for the various combinations of thermocouple materials are based upon their performance in air. Although it has not been shown that a reducing atmosphere, in itself, necessarily contaminates or alters the thermoelectric properties of thermocouple materials, it is nevertheless generally observed that exposure of thermocouples to such atmospheres is accompanied by contamination or changes in the chemical composition which seriously alter the thermoelectric properties. In order to obtain the best performance of thermocouples, it appears necessary to maintain them in an atmosphere having essentially the same composition as air. Consequently the selection of a proper protection tube, which will protect the thermocouple from vapors, fumes, or furnace gases, is sometimes as important as the selection of the thermocouple materials.

Changes in thermoelectric characteristics result from causes such as the following:

(1) metals (solid, liquid, or vapor) coming into contact with the thermocouple materials and altering their chemical composition;

(2) furnace gases and fumes coming into contact with the thermocouple materials (sulfur and sulfur compounds are particularly deleterious);

(3) materials normally stable in an oxidizing atmosphere coming into contact with the thermocouples in a reducing atmosphere; one common cause of contamina-

tion, which is serious in the case of rare-metal thermocouples, is the reduction of silica (usually present in insulating and ceramic protection tubes) to silicon, which readily combines with the thermocouple materials;

(4) preferential oxidation and reduction of base-metal alloys exposed alternately to oxidizing and reducing atmospheres; this results in a gradual change in chemical composition, because all the elements which comprise an alloy are not oxidized and reduced at the same rates under all conditions.

Many types of protection tubes are required in order to meet all needs. In many cases, the conditions under which thermocouples are used are such that two tubes are required to provide the desired protection. For instance, a primary tube of porcelain or fused silica may be placed inside a secondary tube of metal, silicon carbide, or fireclay. The primary tube of low volatility is intended to provide imperviousness to gases at high temperatures, and the secondary tube to provide resistance to thermal and mechanical shock and to corrosion.

In thus providing protection for the thermocouple, however, one should not lose sight of the fact that a thermocouple can perform its function only when the conditions of heat transfer are such that the measuring junction attains, or at least approaches, the temperature to be measured. When a tube of large cross-section or more than one tube is used, particularly if the tubes have a high thermal conductance, it should be carefully considered whether the depth of immersion is sufficient to insure that the temperature of the thermocouple junction is reasonably close to the temperature to be measured. Short, thick-walled tubes may cool the junction so much that the indications are comparatively worthless.

Platinum to platinum-rhodium thermocouples are particularly susceptible to contamination and should be protected by ceramic tubes which are impervious to gases and vapors at all operating temperatures. Metal protection tubes usually provide sufficient protection for base-metal thermocouples. The oxide coatings on the thermocouple wires are fairly effective in protecting the wires from contamination by metallic vapors. Metal tubes which provide sufficient protection in an oxidizing atmosphere may be entirely unsatisfactory if large amounts of furnace gases are present. In some installations it has been found advisable to ventilate the interior of the protection tube with a slow stream of air to minimize the deleterious effects of furnace gases.

The primary ceramic tubes which meet most requirements of stability and imperviousness to gases are: highly refractory porcelain, sometimes called "Sillimanite" or "Mullite" for temperatures up to about 1550 °C (2800 °F), fused silica for temperatures up to about 1050 °C (1900 °F) in an oxidizing atmosphere, and "Pyrex" glass for temperatures up to about 600 °C (1100 °F).

The secondary or metal tube most suitable for a particular application depends to a large extent upon the type of corrosion encountered. Nickel-chromium-iron tubes are particularly useful in oxidizing atmospheres, chromium-iron tubes in atmospheres containing sulfur, and nickel or iron tubes in hot caustic and molten metal baths. The temperature limits given in Table 3 for the various types of tubes are those which will, in general, result in a reasonably long life. The tubes may be used at higher temperatures than those given, but higher operating temperatures will result in a shorter life.

Fireclay, silicon carbide, and graphite meet certain requirements of secondary tubes at temperatures above the useful limits of metal tubes. Numerous other types of tubes have been developed for specific purposes. Recommendations regarding tubes for any particular purpose may be obtained from pyrometer manufacturers.

Table 3. Recommended Maximum Operating Temperature of Metal Protection Tubes.

	commended Maximu	nperature
Type of Tube	(°C)	(°F)
Seamless steel	550	1000
Wrought iron	700	1300
Cast iron	700	1300
Calorized wrought iron	800	1500
14-per cent chromium iron	800	1500
28-per cent chromium iron	1100	2000
18 (Cr)-8 (Ni)- stainless steel	850	1600
32 Ni-20 Cr-48 Fe	1100	2000
62 Ni-13 Cr-25 Fe	1150	2100
Nickel	1100	2000

X. Calibration of Thermocouples

Various methods used for calibrating thermocouples and of testing thermocouple materials and the precautions which must be observed in order to attain various degrees of accuracy are given in a separate paper, which is essentially the same text as the paper entitled "Methods of Testing Thermocouples and Thermocouple Materials" published originally in the *Journal of Research of the National Bureau of Standards*.[13] The numerical values in the original text have been brought into agreement with data published later.

XI. Measurement of Temperatures

The measurement of the temperature of any particular object or space is in many cases a problem in itself, even after a suitable thermocouple has been selected and calibrated. The methods employed in many instances are described elsewhere in this symposium. However, there are certain fundamentals that must be observed in any case.

The temperature indicated by a thermocouple is that of its measuring junction, but usually this is of no interest in itself. The accuracy obtained in measuring the temperature of any object or space usually depends upon how closely the junction of the thermocouple can be brought to the same temperature as that of the object or space, or to some temperature which is definitely related to that of the object or space.

If under steady conditions there is a net exchange of heat between the thermocouple junction and an object, then there is a difference in temperature between the two. The magnitude of this difference in temperature depends upon the rate of heat transfer and the thermal resistance between the junction and the object. The idea is to bring the thermocouple junction into as good thermal contact as possible with the object, and to insulate the junction as well as possible against the transfer of heat to or from other objects or spaces. Greater precautions are obviously necessary in accurate measurements than in rough ones.

As an illustration, suppose we desire to measure the temperature of a metal plate which is heated from within by some means. The bare thermocouple junction is brought into contact with the metal plate. The junction will receive some heat from the plate by thermal conduction, and probably a smaller amount by radiation and convection. The junction will lose heat by conduction along the thermocouple wires, and by convection, conduction, and radiation to the surroundings. Obviously the junction will be at a lower temperature than the plate. However, this difference in temperature can be reduced:

- (A) by improving the thermal contact:
  - (1) by flattening the junction to obtain a larger area of contact, or better still
  - (2) by soldering, brazing, or welding the junction to the plate;
- (B) by reducing the heat loss from the junction:
  - (1) by keeping the wires close to the plate for some distance so as to reduce the temperature gradient in the wires near the junction, and/or
  - (2) by raising the temperature of the space immediately surrounding the junction:
    - (a) by insulating the junction from that space, or
    - (b) by utilizing an auxiliary source of heat as is done in the compensated contact thermometer.[14, 15]

The thermocouple junction may be at either a higher or lower temperature than the object depending upon the direction of the net heat transfer. The use of thermocouple protection tubes usually makes it more difficult to bring the thermocouple junction to nearly the same temperature as that of an object, because of the additional thermal resistance introduced between the junction and object and the additional transfer of heat along the protection tubes. For example, the junction of a thermocouple may be brought within a few hundredths of a degree of the temperature of a liquid by immersing the bare wires in the liquid for a distance of 5 to 10 diameters of the wire, whereas if a protection tube is used with the thermocouple it will be necessary to immerse the junction 5 to 10 diameters of the protection tube to obtain the same degree of accuracy. In most applications, the best that can be done is to bring the thermocouple junction and object as close together as possible and immerse the thermocouple as far as practicable in the heated medium.

In the measurement of certain temperatures, particularly those of small objects and materials of low thermal conductivity, consideration must be given to the possibility that the temperature to be measured may be altered by the introduction of the temperature-measuring device.

In the measurement of temperatures varying with time, heat capacity of thermocouples and protecting tubes as well as thermal contacts are involved. If the temperature is rising, the temperature of the junction itself will at any instant be lower than that of the surroundings. The reverse will be true if the temperature is falling. This is referred to as thermal lag. By appropriate auxiliary measurements, however, it is usually possible to determine the lag[16] under the particular conditions of use, and apply corrections to the thermocouple readings.

XII. Installations

The cost of pyrometer equipment is great enough to warrant installing it, not only so that the desired temperature can be measured with the required accuracy but also in such a manner as to protect the equipment, as far as practicable, from changes and deterioration. The installation of simple pyrometer equipment for more or less temporary service in an air-conditioned laboratory, far removed from the vibrations set up by heavy equipment such as trip hammers, rolling mills, etc., is a comparatively simple matter. However, in the large installations required in many industrial plants, every precaution should be taken to protect the thermocouple, wiring, and instruments from the various deleterious conditions which may seriously affect their accuracy and life.

1. General Precautions. The installation of extensive thermocouple equipment requires the services of competent electricians. Just as much attention, if not more, should be given to the wiring, switches, switchboards, etc., as is given in the case of ordinary power installations. Proper fixtures should be used to mount the thermocouples in the furnaces. Lead wires should have a weatherproof covering and should be run in a metal conduit except possibly for a short length of flexible cable at the ends of the conduit. The conduit should be grounded to prevent leakage from power installations or lighting circuits. All joints in the lead wires should be soldered and taped. When indicators or recorders of low resistance are employed, it is of the greatest importance to have a well-constructed electrical installation to insure a constant line resistance. Since instruments of low resistance are usually calibrated for a low line resistance of definite value, special attention must be given to contact resistances at switches. Frequently switches rated at 100 amperes are required, although the actual thermoelectric current is only a few milliamperes. If the indicator is of high resistance, or operates upon the potentiometric principle, the factor of very low line resistance is not of great importance, but the wiring should be well installed, to avoid large changes in the resistance. Stationary indicating and recording instruments usually should be mounted upon switchboards, with suitable selective or commutating switches when several thermocouples are to be used with one indicator. When the junction between the thermocouple and leads is exposed to severe conditions, rain, etc., as in outside kilns, a weatherproof terminal head should be used. This consists of an outside casing which fits over both binding posts. The cover may be tapped for conduit wiring or provided with a packing gland or stuffing box if a length of flexible cable is used between the thermocouple and the conduit.

The indicator or recorder should be conveniently located. If the instrument is desired especially for the use of the operator of a furnace, it should be placed where it is readily visible. It should be mounted where vibration and excessive dirt and dust will not injure delicate parts of the mechanism. In almost all industrial installations an outside protecting case is required to prevent dust from filtering through the case of the indicator. Special devices are employed to damp out vibration when this is serious, as in the neighborhood of a trip hammer or rolling mill. Frequently the instruments are suspended on "vibration-proof" mountings.

2. **Location of Thermocouples.** The proper location of the thermocouple in a furnace depends upon the particular process and the use to which the furnace is put. The primary consideration is to locate the measuring junction so that it acquires the temperature which it is desired to measure. This requires taking into consideration the thermal lag and heat transfer to and from the thermocouple junction. Both of these factors are materially affected by protection tubes. A secondary consideration, however, is to locate the thermocouple where the lead wires may be conveniently located. The space between the protecting tube and the furnace wall should be plugged with refractory cement, so that hot air cannot strike through the hole onto the terminals of the thermocouple, nor cold air be drawn in, thus cooling the measuring junction of the thermocouple.

3. **Common Return.** The use of a common return wire for a multiple installation is in general unsatisfactory. When grounds or short circuits occur at any point between the measuring junctions and the instrument--for example, between the common return and the other lead wire of one thermocouple—all the thermocouples on the common return have, in addition to their own emf, an impressed potential drop due to the current flowing in the shorted thermocouple. This may cause a large error in the reading of every thermocouple in the system. With the common return, leakage from a power installation affects the readings of every thermocouple connected to the return and a leakage through a high resistance may alter the readings of every thermocouple by the same amount so that the presence of such

leaks is not always readily detected. It is also possible, by leakage from different thermocouples to the ground, to obtain very erratic and erroneous readings when the common return is employed. The insulation resistance of materials becomes very low at high temperatures, making it difficult to insulate the various thermocouple wires from one another and from the furnace parts, even when individual returns are used. Base-metal thermocouples are frequently constructed with the measuring junction welded to the end of the metal protecting tube in order to reduce thermal lag. Even when the thermocouple is not welded at this point, the measuring junction usually touches the protecting tube and is in good electrical contact with it. If a common return is used when the thermocouples are mounted in this way, any electrical connection or leakage between the metal protecting tubes (through the furnace structure, etc.) will produce serious errors. However, if individual returns are used, the metal protecting tubes need not be insulated from one another. The troubles ordinarily encountered with common return installations are sufficient to warrant the extra cost of the wire required to install individual thermocouple circuits.

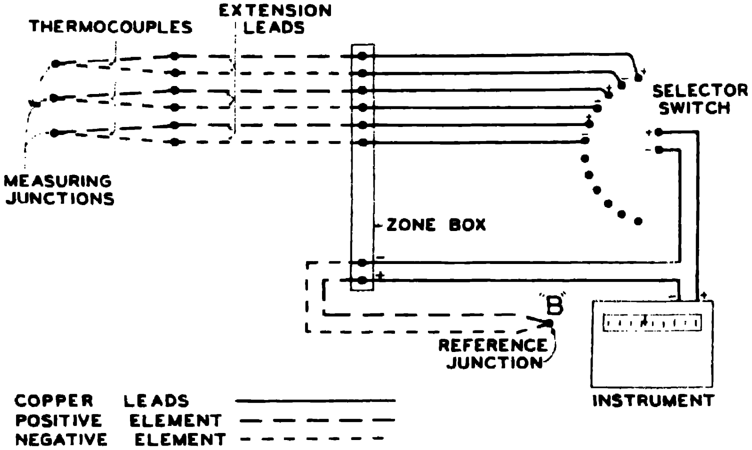

FIG. 8. Connections between several thermocouples and a distant instrument.

4. Use of a Zone Box. Extension lead wires are rather costly and should not be employed extravagantly. Also the use of long lengths of extension leads increases the line resistance, since the resistivity of the lead materials is much higher than that of copper.

For an installation in which several thermocouples are connected through a selector switch to an instrument located at some distance from a furnace, a wiring scheme similar to that shown in Fig. 8 may be very useful in saving extension lead wire and consequently in reducing the cost and resistance of the line. The common reference junction "B" for each thermocouple can be located at any conveniently controlled point or at the instrument if the latter is equipped with an automatic reference junction compensator by running only one pair of extension leads from the zone box to the controlled point or the instrument. A zone box is a box or zone of uniform temperature which need not be measured or maintained constant. It should be pointed out that although a common reference junction is used for all the thermocouples, the system is not subject to any of the objections which have been raised against the use of a common return.

5. Thermocouples Purposely Insufficiently Immersed. In many processes a furnace is operated at such a high temperature that a thermocouple or protecting tube cannot withstand the severe conditions inside the furnace. In this case the thermocouple may be advantageously inserted only part way through the furnace wall, or flush with the inner wall of the furnace. The temperatures indicated by thermocouples installed in this manner are always lower than those of the furnace interior, but they may bear a fairly definite relationship to the temperature of the furnace, and hence the method may be satisfactory for temperature control and reproduction of furnace conditions from day to day.

6. Measurement of Average Temperature. It is frequently desirable to measure "the average temperature" of an object or a heated space by using thermocouples. No discussion of what is meant by the average temperature of an object or space or why anyone would be interested in measuring any such average will be given here. The average temperature that can be measured with thermocouples is only a mean of the temperatures of the measuring junctions of a number of thermocouples. This average may or may not be a close approximation to the average temperature which one desires to measure, depending upon such factors as the temperature distribution, the number and location of the thermocouples, etc.

If the measuring junctions of a number of thermocouples are placed in thermal contact with an object or located in a heated space, the average temperature of the junctions may be obtained by any one of three methods: (1) by reading the thermocouples individually and averaging the readings; (2) by connecting them in series and reading the total emf: or (3) by making all the thermocouples of equal resistance and connecting them in parallel so that the average emf is read directly. Although each of these methods has certain practical advantages over the others, they are all equivalent in that one is no more accurate than the others and that the same average temperature (that of the junctions) is measured in each case. In the following discussion, it will be assumed that the temperature-emf relations of all the thermocouples used in any one case are identical, and that any correction or compensation required for the reference junctions is properly cared for.

The important advantages of taking readings of the individual thermocouples are that (1) one obtains not only the average temperature but also some idea of the temperature distribution; (2) the thermocouple junctions may be placed in contact with or welded to metal objects, thus insuring good thermal contact; and (3) the failure of any individual thermocouple is immediately detected. The disadvantage is that several observations must be taken, requiring several instruments if the observations are to be taken simultaneously or considerable time, during which the temperatures may change if the observations are to be taken with one instrument.

One may average the values of the emf of the individual thermocouples and obtain the average temperature from the average emf, or one may average the temperature values obtained for each thermocouple. The average values obtained in these two different ways will not necessarily agree exactly because of the fact that the emf of a thermocouple is not a linear function of the temperature. If the temperature gradients in the object or heated space are not very large (less than about 50 °C) the difference in the averages obtained in the two different ways is usually insignificant. If the temperature gradients in the object or heated space are so large (several hundred degrees) that there is an appreciable difference in the average temperature obtained in the two different ways, the average temperature obtained by using thermocouples located at several selected points probably has no exact significance.

Because of the fact that values of temperature may be obtained with the individual thermocouples and averaged with this method, it is not necessary to use thermocouples with approximately the same temperature-emf relation.

The important advantage of connecting the thermocouples in series or in parallel is that only one observation is required to obtain the average emf of a number of thermocouples. However, such a single observation yields no information regarding the temperature distribution in the object or space. Connecting the thermocouples according to either method requires that the thermocouple wires and measuring junctions be electrically insulated from one another. This makes it difficult under certain conditions to bring the junctions into good thermal contact with an electrically conducting medium.

The objections to connecting a number of thermocouples in series are:

(1) the emf developed by the thermocouples in series may be too great to be measured with the instruments available; (2) a short circuit which might materially reduce the emf of one of the thermocouples would not be detected by a single observation of the total emf.

It can be shown by applying Kirchhoff's laws that the potential difference across the terminals of a number of thermocouples of equal resistance connected in parallel is the average of the emfs of the individual thermocouples. Inasmuch as the average emf is measured directly when the thermocouples are connected in parallel, the emf can be measured with any instrument that is used for measuring the emf of a single thermocouple.

It should be pointed out that the temperature indicated when the two individual thermocouple wires are attached to a metal object at two points which may be designated P and Q (so that the electric circuit is completed through the metal), depends upon the thermoelectric power of the metal with respect to the thermocouple wires and is not necessarily the temperature of the metal at any point between P and Q, and consequently is not the average temperature of the metal between P and Q except in very special cases. If the metal to which the thermocouple wires are attached is thermoelectrically positive to one element of the thermocouple and negative to the other, the temperature measured will be somewhere between those of P and Q. The thermocouple will indicate a temperature approximately midway between those of P and Q only if the metal is approximately midway between the two thermocouple wires thermoelectrically.

It is readily seen that if the wires of an iron-Constantan thermocouple are attached to a piece of iron, the temperature measured will be that where the Constantan wire is attached, and if they are attached to a piece of Constantan the temperature measured will be that where the iron wire is attached.

If the metal to which the thermocouple wires are attached is thermoelectrically positive or negative to both wires of the thermocouple, the value of the temperature indicated will not be between those of P and Q. For example, suppose that the wires of a platinum to 90 platinum-10 rhodium thermocouple are attached to a piece of constantan, and that the temperature of the point where the platinum wire is attached is 700 °C and that where the platinum-rhodium is attached is 750 °C. Let the reference junctions of the thermocouple be at 0 °C. The circuit is equivalent to a 90 platinum-10 rhodium to constantan thermocouple with its junctions at 750° and 0 °C in series with a constantan to platinum thermocouple with its junctions at 700° and 0 °C. The resultant emf developed in the circuit will be approximately 9.14 mv which corresponds to 962 °C for the platinum to 90 platinum-10 rhodium thermocouple.

XIII. Conclusion

In conclusion the author would like to emphasize that the success attained in the measurement of temperatures with thermocouples depends primarily upon the ability of the observer to bring the junctions of the thermocouples to the desired temperatures and upon the stability of the thermocouple materials. The reader's attention is directed to a number of papers in this symposium which deal with (1) the measurement of temperatures in particular cases, (2) the stability of thermocouples, and (3) the instruments available for use with thermocouples in the measuring, recording, and controlling of temperatures.

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The Calibration of Thermocouples at Low Temperatures

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Introduction

Although the platinum resistance thermometer is used to define the International Temperature Scale in the range 0 to −190 °C, copper-constantan thermocouples are extensively used for temperature measurements in this range. A thermocouple may be calibrated either by direct comparison with a standard platinum resistance thermometer at several temperatures, or by determining its emf at a number of fixed points, the temperatures of which are known on the International Temperature Scale. After having obtained values for the emf and temperature at a number of calibration points, the process of interpolating, to obtain a continuous temperature-emf relation over the whole range, is greatly facilitated by the use of a table giving the emf of a representative thermocouple. Such a table for a copper-constantan thermocouple is given in this paper. It is the purpose of this paper to describe first the apparatus and methods used at the National Bureau of Standards to calibrate thermocouples by direct comparison with a platinum resistance thermometer, and then to show how, with considerably simpler apparatus, certain fixed points may be used to obtain a calibration of sufficient accuracy for most purposes.

Calibration by Comparison with a Platinum Resistance Thermometer

The strain-free platinum resistance thermometer is used as the standard temperature-measuring instrument for the calibration of thermocouples in the range 0 to −190 °C, although at temperatures near the normal boiling point of oxygen (−182.97 °C) the oxygen vapor-pressure thermometer may be used. At the low end of this range a bath of liquid air or liquid oxygen boiling at atmospheric pressure is used to cool a copper comparison block into which the thermocouple junction and the standard thermometer are inserted. For calibrations in the temperature range above −170 °C a cryostat[1] is used which automatically maintains the desired constant temperature in a stirred liquid bath. A vertical section of the cryostat is shown in Fig. 1. The refrigeration is supplied by liquid air in the outer Dewar flask, *C*, and is controlled by varying the gas pressure between the walls of the inner Dewar, *D*, which contains the constant-temperature bath. This method of applying and controlling the refrigeration was previously used by Rothe[2] and by Keyes, Taylor and Smith.[3] The gas pressure is adjusted through the tube *M*, which connects with a high-vacuum system.

The cryostat liquid is circulated by a propeller, *I*, which revolves in the bottom of a Bakelite tube, *P*, in such a direction that the liquid passes up through the inside of the Bakelite tube and down the outside. To permit this circulation, four windows, *B*, 2.5 cm long were cut in the Bakelite tube. In order that the liquid at the surface shall be circulated, and a stagnant region avoided, the liquid level is kept below the top of the windows. The propeller is driven at a speed of about 400 revolutions per minute, through a system of three gears, *H*, driven by shaft, *K*, connecting to a motor through a flexible shaft, *O*. Three vertical vanes, *F*, support the bearings for the propeller and idler gear shafts and improve the circulation by preventing a whirling motion of the liquid above and below the propeller.

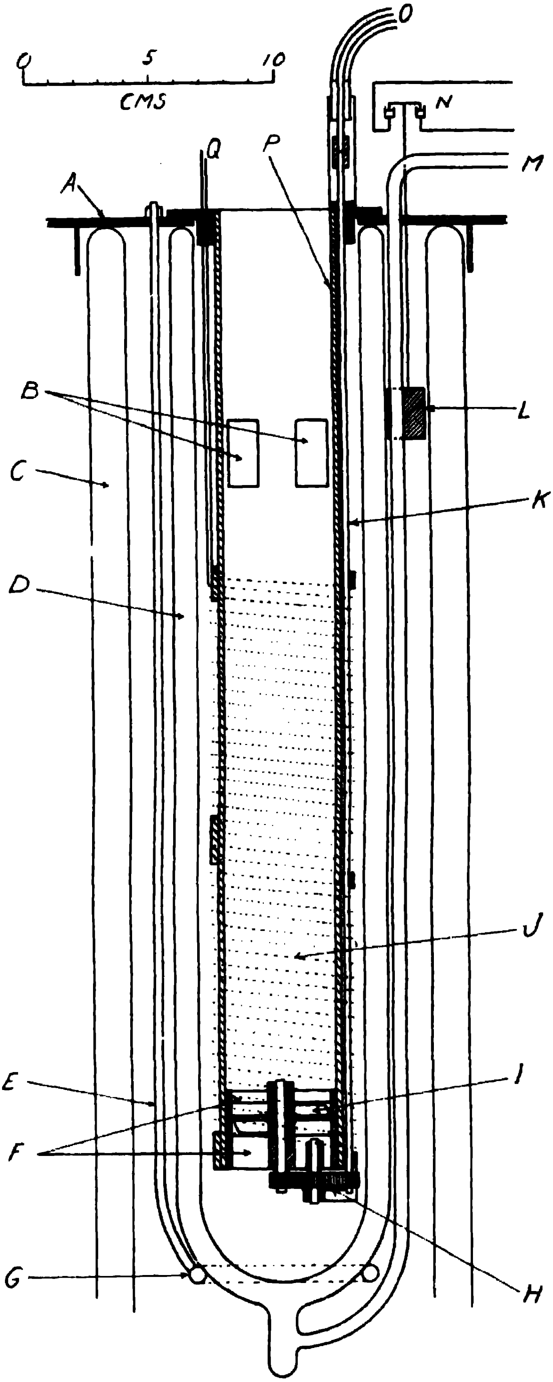

FIG. 1.

Vertical section of the cryostat.

Stainless steel pinions and a Bakelite idler gear were found to be satisfactory. Monel metal shafts turning in high lead (85 per cent) babbitt bearings were used. Since the cryostat liquids used are poor lubricants, powdered graphite was rubbed on the bearing surfaces before assembling. Special bearing materials consisting of a mixture of graphite in metal may be more satisfactory.

The heating coil, *J*, shown by dotted lines, is made of No. 22 B & S gage Nichrome wire and has a resistance of about 30 ohms. The bare wire is wound bifilarly on a form which fits the stirrer tube, *P*, its ends terminating at the top in leads, *Q*, which connect to the power supply through the thermoregulator. The form is made from a Bakelite tube by cutting wide slots in its walls, leaving six strips about 1 cm wide and supporting rings at the ends and center. Lag in the heater is reduced by this support and manner of winding, which separates the heater coil from the tube, *P*, and allows the bath liquid to circulate on all sides of the wire. It is advantageous in compensating for an excess of refrigeration to have the heating surface close to and distributed over the refrigerating surface.

The thermoregulator consists of a coil of bare platinum wire immersed in the bath just above the propeller, and connected to a Wheatstone bridge as a three-lead, Siemens type resistance thermometer. The mirror of the galvanometer in the Wheatstone bridge circuit reflects a beam of light from an indandescent lamp, forming an image of the filament on the edge of a screen placed just in front of a photoelectric cell. If the bath is too cold the image moves onto the sensitive plate of the photocell; if too warm it moves off. When the cell is illuminated, the photoelectric current, amplified, actuates a relay which short-circuits a variable external resistance in series with the heating coil in the cryostat, increasing the heating current. The potential across the heater circuit is adjusted so that, when the relay contacts are open, the bath is slowly cooling, and when they are closed the bath temperature is slowly rising. The sensitivity of the thermoregulator may be increased almost without limit by increasing the current through the Wheatstone bridge circuit which contains the platinum resistance element. The constancy of the temperature of the bath, therefore, is not limited by the sensitivity of the thermoregulator. However, the finite time required for the temperature of the bath to respond to the demand of the thermoregulator causes the temperature to oscillate slightly above and below the mean. The amplitude of these oscillations may be made small by adjusting the heating current so that only a small increment is controlled by the thermoregulator. This increment must be large enough to take care of irregularities of heat conduction into the bath. It is not difficult to adjust the apparatus to maintain a temperature constant to ±0.005 °C, and by careful manipulation the oscillations may be made smaller than ±0.001 °C. In some photoelectric thermoregulator circuits thyratron tubes are used instead of mechanical relays. The thermoregulator described here was put into operation before thyratrons came into general use. It is possible that this circuit may, with profit, be modified to include a thyratron which controls the heating current.

As far as possible, the non-flammable mixtures recommended by Kanolt[4] are used for the cryostat liquid. For temperatures down to −75 °C the liquid used is the eutectic mixture of carbon tetrachloride and chloroform (49.4 per cent by weight of CCl_4 and 50.6 per cent of $CHCl_3$), which has a freezing point of −81.4 °C as determined by Kanolt. For temperatures between −75 and −140 °C, a 5-component mixture containing 14.5 per cent of chloroform, 25.3 per cent of methylene chloride, 33.4 per cent of ethyl bromide, 10.4 per cent of trans-dichloroethylene and 16.4 per cent of trichloroethylene was used. This mixture freezes at about −150 °C.

At temperatures below −140 °C the non-flammable liquids are so viscous that they cannot be readily stirred. For this lower range the liquid used is commercial propane, which is sold for domestic gas heating under various trade names. The propane, which is a gas at atmospheric pressure and room temperature, is compressed into steel cylinders and liquefied at room temperature at a pressure of about 150 lb per sq. in. It may be conveniently liquefied at atmospheric pressure by running it through a copper coil immersed in liquid air. Its boiling point is about −44 °C and it remains liquid down to liquid air temperatures. It is, however, highly flammable and its use is attended with some danger. Every precaution should be taken to prevent the mixing of liquid air and propane in case the Dewars break. The inner Dewar should be fitted with either a metal liner or a metal jacket if propane is used. If liquid nitrogen is available it should be used instead of liquid air for the refrigerating liquid.

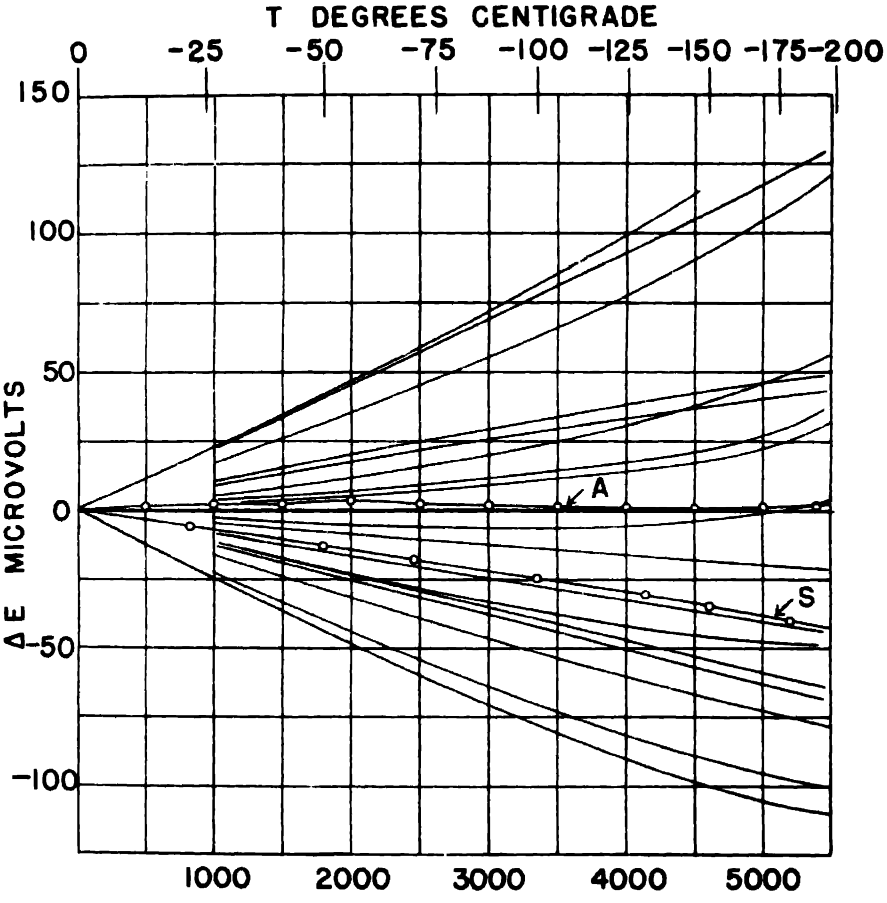

FIG. 2. Differences between the emfs of some copper-constantan thermocouples and the values given in Table 1.

Table 1. Reference Table for Copper-Constantan Thermocouples.

Temp. (°C)	E (μv)	dE/dt (μv per °C)	Temp. (°C)	E (μv)	dE/dt (μv per °C)	Temp. (°C)	E (μv)	dE/dt (μv per °C)
0	0.0		−32	1182.8		−64	2263.4	
		38.4			35.3			32.0
−2	76.8		−34	1253.4		−66	2327.4	
		38.2			35.1			31.8
−4	153.2		−36	1323.6		−68	2391.0	
		38.0			34.9			31.6
−6	229.2		−38	1393.4		−70	2454.1	
		37.8			34.7			31.3
−8	304.8		−40	1462.8		−72	2516.7	
		37.6			34.5			31.1
−10	380.1		−42	1531.8		−74	2579.0	
		37.4			34.3			30.9
−12	455.0		−44	1600.4		−76	2640.8	
		37.3			34.1			30.7
−14	529.5		−46	1668.6		−78	2702.1	
		37.1			33.9			30.5
−16	603.7		−48	1736.3		−80	2763.1	
		36.9			33.7			30.2
−18	677.4		−50	1803.7		−82	2823.5	
		36.7			33.5			30.0
−20	750.8		−52	1870.6		−84	2883.6	
		36.5			33.3			29.8
−22	823.8		−54	1937.2		−86	2943.1	
		36.3			33.0			29.6
−24	896.3		−56	2003.3		−88	3002.3	
		36.1			32.8			29.3
−26	968.5		−58	2068.9		−90	3061.0	
		35.9			32.6			29.1
−28	1040.3		−60	2134.2		−92	3119.2	
		35.7			32.4			28.9
−30	1111.8		−62	2199.0		−94	3176.9	
		35.5			32.2			28.7

For the measurement of the emf of the thermocouple a low-range Wenner potentiometer is used. This instrument has two ranges: 0 to 11,000 μv in steps of 0.1 μv, and 0 to 110,000 μv in steps of 1 μv. Switches are provided for reversing simultaneously the potentiometer current and the emf being measured, so as to cancel out spurious emfs in the galvanometer circuit. Also, the leads from the potentiometer to the thermocouple may be shorted at the ice junctions to check the measuring circuit at zero emf.

A Reference Table for Copper-Constantan Thermocouples

It has been found that the temperature-emf relation for a copper-constantan thermocouple, in the range 0 to −190 °C may be expressed by the equation

$$E = at + bt^2 + ct^3$$

where E is the emf, t is the temperature in degrees centigrade and a, b and c are constants. A thermocouple made of carefully selected wire was calibrated at approximately 10-degree intervals over this range of temperatures. The constants a, b and c were computed by the method of least squares. The observed points deviate randomly from the equation so obtained, the average deviation being 0.6 microvolt. As a convenience in calibrating and using thermocouples, Table 1 was computed, giving the emf at two-degree intervals. This permits an accuracy of interpolation of 0.1 microvolt. Calibrations are made by determining the emf at a

Table 1.—(*Continued*)

Temp. (°C)	E (μv)	dE/dt (μv per °C)	Temp. (°C)	E (μv)	dE/dt (μv per °C)	Temp. (°C)	E (μv)	dE/dt (μv per °C)
-96	3234.3	28.4	-128	4087.5	24.6	-160	4815.4	20.6
-98	3291.1	28.2	-130	4136.7	24.4	-162	4856.6	20.3
-100	3347.5	28.0	-132	4185.5	24.1	-164	4897.2	20.1
-102	3403.4	27.7	-134	4233.8	23.9	-166	4937.3	19.8
-104	3458.9	27.5	-136	4281.5	23.6	-168	4976.9	19.5
-106	3513.9	27.3	-138	4328.8	23.4	-170	5015.9	19.3
-108	3568.4	27.0	-140	4375.6	23.1	-172	5054.5	19.0
-110	3622.5	26.8	-142	4421.8	22.9	-174	5092.5	18.7
-112	3676.1	26.6	-144	4467.6	22.6	-176	5129.9	18.5
-114	3729.2	26.3	-146	4512.9	22.4	-178	5166.9	18.2
-116	3781.8	26.1	-148	4557.6	22.1	-180	5203.3	17.9
-118	3834.0	25.8	-150	4601.9	21.9	-182	5239.1	17.6
-120	3885.6	25.6	-152	4645.6	21.6	-184	5274.4	17.4
-122	3936.8	25.4	-154	4688.8	21.3	-186	5309.2	17.1
-124	3987.5	25.1	-156	4731.4	21.1	-188	5343.4	16.8
-126	4037.8	24.9	-158	4773.7	20.8	-190	5377.1	16.6
						-192	5410.2	

few temperatures and plotting deviations from the table. Deviation curves for a number of copper-constantan thermocouples are shown in Fig. 2. Each of these curves represents from 5 to 10 observed points. This is more points than are necessary for a calibration, but in this case closer spacing of the observations was needed so that irregularities in the deviation curves might be detected. Ordinates are emf of thermocouple minus emf from Table 1. The observed emf is used as abscissa because the deviation curves so obtained are more nearly linear than those obtained using abscissa to represent temperature. The deviation curves of thermocouples sent in for calibration are distributed almost equally above and below the axis. The curves are smooth, of slight curvature, and have no inflection points. Also shown in the figure are deviation curves of two other copper-constantan thermocouple tables as given by Adams [5] and Southard and Andrews,[6] labeled "*A*" and "*S*," respectively. Adams' table gives values which differ by only 3 microvolts (maximum) from Table 1, but it has been found that most of the thermocouples calibrated at the National Bureau of Standards show somewhat more regular deviation curves from Table 1 than from Adams' table. The thermocouple wires range in size from No. 22 to No. 36 B & S gage, sizes which are ordinarily used at low temperatures. The table of Southard and Andrews gives emfs considerably lower than the average for the thermocouples tested.

Calibration at Fixed Points

1. The CO_2 Point. The deviation curves of all the thermocouples that have been calibrated are so nearly straight that a determination of the emf at the normal sublimation temperature of carbon dioxide (−78.51 °C on the International Scale) is sufficient to establish the temperature-emf relation in the range 0 to −90 °C. An accuracy of ±2 microvolts may be obtained by plotting the deviation curve in the manner shown in Fig. 2 and drawing a straight line through the observed point and the origin. Since solid carbon dioxide is now a widely distributed commercial product, many laboratories should find it useful as a means of realizing the normal sublimation temperature as a calibration point or as a check point for thermometers and thermocouples. However, certain precautions are necessary to obtain acceptable results. As solid carbon dioxide is usually handled it is seldom surrounded by an atmosphere of pure CO_2 vapor; hence its temperature is considerably lower than the normal sublimation temperature. The temperature is that at which solid carbon dioxide has a vapor pressure equal to the partial pressure of the CO_2 vapor in the atmosphere immediately surrounding the solid. If a Dewar flask is filled with crushed solid CO_2, its initial temperature will be several degrees below the normal sublimation temperature. The temperature will rise slowly with time, as the evaporated vapor washes out the air; and, if diffusion of air into the flask is prevented, it will eventually reach the temperature at which the vapor pressure of CO_2 is equal to the pressure of the atmosphere. Fig. 3 shows some measurements made with a platinum resistance thermometer in such a bath.

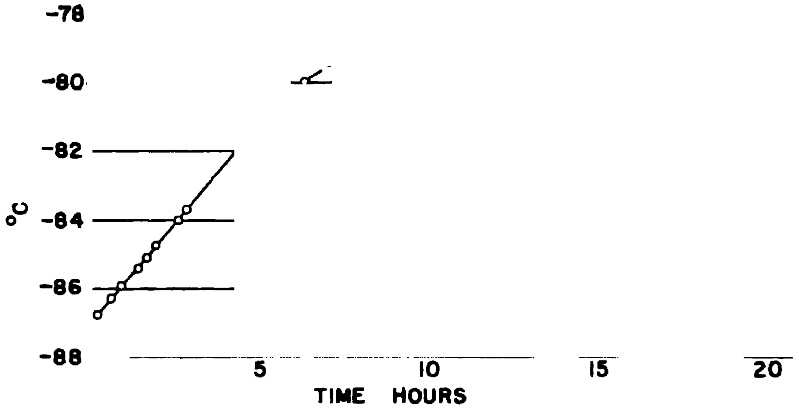

FIG. 3. The temperature of crushed solid carbon dioxide in a Dewar flask.

It is common practice to use a mixture of solid CO_2 in a low-freezing liquid. J. and A. Zeleny[7] made measurements of the temperature of such baths, using solid CO_2 obtained by allowing liquid from a cylinder to escape and collecting the "snow" that is formed in the process. However, it has been found that mixtures of crushed solid CO_2 and liquid do not behave very differently from solid CO_2 alone. That is, they all exhibit an initial low temperature and a gradual rise in temperature. Moreover, the equilibrium temperature of the mixture, at a point below the surface of the liquid, is affected by the hydrostatic pressure of liquid at this point. Thus, the temperature read by the thermocouple or thermometer depends upon the depth of immersion. Also, convection may cause disturbances in the temperature by transporting masses of liquid from one level to another having a different equilibrium temperature.

The quickest and most convenient method we have found is to use crushed solid CO_2 without a liquid, but with an electrical heating coil buried in the solid CO_2 near the bottom of the Dewar flask about 5 cm below the thermometers. An experiment with such an arrangement showed the following results. Starting at a temperature 6 degrees low, 30 watts in the heater caused the equilibrium temperature to be attained in 12 minutes. Further heating caused no change in temperature. The heat input was then reduced and left at 7 watts so as to keep a stream of CO_2 vapor flowing out of the flask to prevent air from diffusing in. Readings were then taken on two platinum resistance thermometers in the bath, and on the barometer in the same room. The temperature of the solid carbon dioxide was calculated from its vapor pressure (barometric) by means of the equation

$$\log_{10} p = 9.81137 - \frac{1349}{t + 273.16}$$

where t is in degrees centigrade and p in mm Hg. The constants in this equation were chosen to fit the results of Meyers and Van Dusen [8] in the neighborhood of the normal sublimation temperature. The results are given in Table 2. From these results it appears that the temperature of equilibrium between solid and gaseous carbon dioxide may be attained by this method with an accuracy of about 0.01 °C. Judging from the evidence available, it appears unlikely that impurities found in commercial solid CO_2 will affect the temperature sufficiently to invalidate this conclusion.

Table 2. The Equilibrium Temperature of Solid CO_2.

Pressure Barometer (mm Hg)	Temperature: Calculated from V.P. Eq. (°C)	Temperature: Res. Therm. I (°C)	Temperature: Res. Therm. II (°C)
754.44	−78.604	−78.598	−78.593

2. The Oxygen Boiling Point. The deviation curves, Fig. 2, indicate that the boiling point of oxygen (−182.97 °C), together with the sublimation point of CO_2, may be used to obtain a fair calibration curve for a copper-constantan thermocouple over the entire range 0 to −190 °C. However, the apparatus necessary for the realization of the oxygen boiling point is more elaborate than that used for the CO_2. Commercial oxygen usually contains enough nitrogen impurity to make the boiling temperature uncertain. Even if the oxygen supply is pure, the liquid oxygen may become contaminated with atmospheric nitrogen by diffusion of air to the liquid surface. Also, the liquid may superheat, in which case the temperature of the liquid in the interior of the bath may be a degree or more above the temperature of the surface. Thus, the temperature of a bath of liquid commercial oxygen cannot be determined simply by reading the barometer and applying a vapor-pressure equation as was done in the case of solid carbon dioxide. A satisfactory method is to use a small quantity of pure oxygen in a vapor-pressure thermometer to determine the temperature of the bath.

It has been found that oxygen of sufficient purity for use in vapor-pressure thermometers may be prepared by the thermal decomposition of potassium permanganate. The procedure is as follows: The salt is outgassed under high vacuum for 17 hours at a temperature of 160 to 175 °C to remove absorbed air. The temperature is then raised slowly while continuing the pumping until, in about 2 hours, the

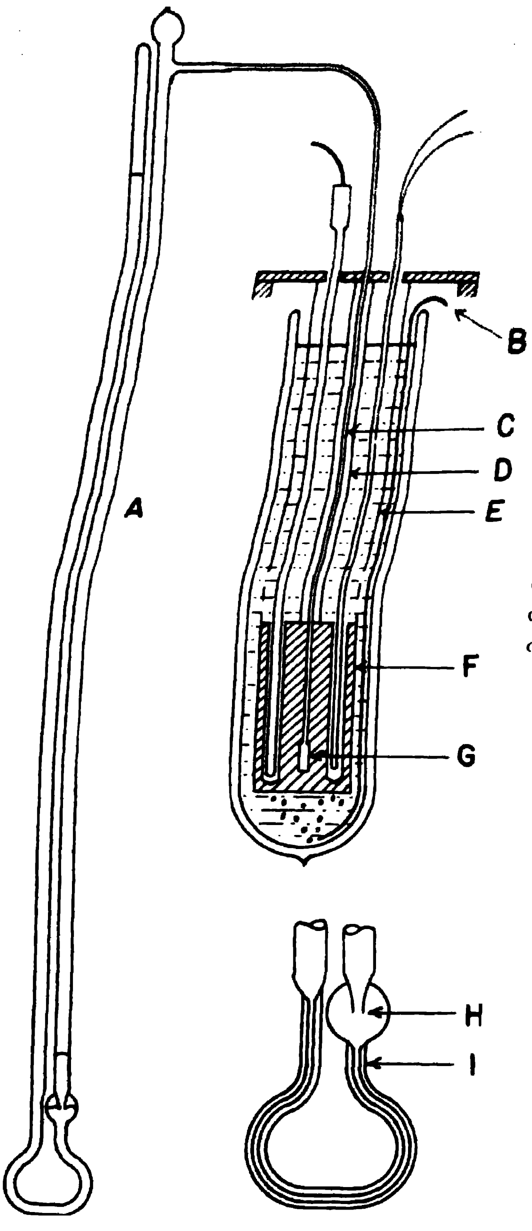

FIG. 4.

Apparatus for the calibration of thermometers and thermocouples at the boiling point of oxygen.

oxygen is coming off at a moderate rate at a temperature of about 215 °C. After discarding the first oxygen generated at this temperature, the rest is collected by allowing it to condense into a bulb surrounded by liquid air. The collection is stopped when the salt reaches a temperature of about 235 °C.

A 4500-cm ^{3} (gas) sample of oxygen thus obtained was distilled in a still having a rectifying column. The distillate was divided into 3 fractions of 300, 4000, and

0 cm.[8] The vapor pressures of these three fractions were compared in an appa-tus equipped with a differential manometer filled with apiezon oil. The maximum fference observed was less than 0.02 mm Hg. at −183 °C. This indicates that ere was no impurity present in the original sample in sufficient quantity to affect e vapor pressure appreciably. The vapor pressure of the oxygen prepared from otassium permanganate was also compared with that of a sample prepared by e electrolytic decomposition[9] of a carefully purified solution of barium hydroxide. t was necessary to use mercury manometers in this comparison because the latter ample was sealed in a vapor-pressure thermometer. The smallest detectable dif-erence was, in this case, 0.1 mm Hg. No difference larger than this was observed.

Several designs of oxygen vapor-pressure thermometers and baths have been sed in the various national standardizing laboratories. The following is a escription of an arrangement now in use at the National Bureau of Standards. n Fig. 4, *F* is a massive copper cylinder immersed in a bath of commercial iquid oxygen. The oxygen from a high-pressure cylinder is liquefied by passing t through a coil of copper tubing immersed in liquid air. The copper cylinder is upported from above by the thin-walled (0.28-mm) Monel cylinder, *E*, which has penings in the sides to permit circulation of the liquid oxygen. The central cavity contains a small quantity of pure liquid oxygen, prepared according to the nethod given above. The vapor pressure exerted by this pure oxygen is trans-nitted to the manometer, *A*, through the copper-nickel tube, *C*. The protecting ube, *D*, keeps the bath from coming into contact with the pressure transmitting ube, *C*, so that cold spots on *C* are avoided. Thus the vapor pressure as read by he manometer is that which corresponds to the temperature of the copper cylinder, nd it is not affected by a possible cold region near the surface of the bath. In rder to prevent superheating of the bath, a slow stream of gaseous oxygen from cylinder is admitted through tube *B* which extends to the bottom of the Dewar lask. The copper cylinder contains wells into which thermocouples or resistance hermometers may be inserted. The copper-nickel tube, *C*, is connected to the Pyrex" glass of the manometer by soldering it to the copper end of a House-eeper[10] seal. The manometer tubing is 1 cm inside diameter. The positions of the mercury menisci are observed by means of a mirror-backed glass scale mounted in contact with the manometer tubes. The precision of measurement is about 0.1 mm. The amount of oxygen in the vapor-pressure bulb and manometer is such that when the copper cylinder is at room temperature the pressure is about 3 atmospheres. Thus the system, after being filled with pure oxygen, may be permanently sealed.

An enlarged view of the bottom of the manometer is shown in Fig. 4 (lower right). This illustrates a method of keeping the manometer clean on the oxygen side. In the usual type of manometer the oxidation of the mercury on the oxygen side darkens the tube and causes a misshapen meniscus, which introduces errors into the measurement of pressure. In this manometer, when the apparatus is not in use, the mercury meniscus stands in the small tube at *I*, presenting only a small surface to the oxygen. When the copper cylinder is cooled and oxygen condenses, the mercury rises and the surface spreads in the bulb so that as the mercury flows into the manometer tube through the constricted tip, *H*, nearly all the oxide is left behind. The ratio of the cross-sectional area of the bulb to that of the tip is about 100 to 1.

The results obtained with this apparatus show a considerable improvement over those obtained using an all-glass vapor-pressure thermometer in a stirred bath of liquid oxygen. It is believed that oxygen point calibrations of platinum resistance thermometers may be made with a reproducibility of about ±0.003 °C. This, of course, greatly exceeds the accuracy needed for thermocouple calibrations.

The Accuracy Obtainable with Copper-Constantan Thermocouples

The accuracy with which copper-constantan thermocouples may be calibrated and used at low temperatures is usually limited by lack of homogeneity of the wires. That is, irregularities in the chemical composition or physical condition of the wires, in regions where temperature gradients exist, cause spurious emfs to appear, which change if the temperature gradient is shifted slightly along the wire. In the copper-constantan thermocouple, the constantan is usually the element responsible for most of the spurious emf, the copper as a rule being relatively uniform. Specimens of constantan have been found in which emfs as large as 10 microvolts appeared when part of the wire was at liquid air temperature and the rest at room temperature. By testing the wire and choosing pieces in which such effects are small, thermocouples may be constructed which are much more dependable than those made of untested wire. Another improvement that is sometimes used is to have several constantan wires in the same bundle, either in parallel, forming with the copper wire a single thermocouple, or in series with an equal number of copper wires forming a multiple-junction thermopile. In both of these arrangements effects of irregularities in the different wires will be partially canceled out. For some purposes it is desirable to protect the thermocouple, or at least those portions of the wires subject to temperature gradients, with a rigid covering, so that handling will not set up strains in the wires. This arrangement, however, defeats one of the principal advantages of thermocouples, that is, their adaptability for use in intricate apparatus from which the wires must be brought out through devious paths. A few thermocouples of special construction, in which several selected constantan wires were used, have been calibrated at low temperatures at the National Bureau of Standards. Although experience with such thermocouples has not been extensive, it is believed that the best of these, when calibrated at intervals of 50 °C or less, and used in conjunction with Table 1, will give results which are in error by less than 1 microvolt. This limit of error is given on the basis of one thermo-junction; for a multiple junction instrument it will be larger, since the emf produced is greater. The effect of inhomogeneities in thermocouple wire, methods of testing the wire, the construction of multiple-junction thermocouples, and general technique of thermoelectric measurements have been treated in detail by White.[11] He is principally concerned with thermocouples for use in calorimetry at moderate temperatures, but a great deal of the technique is applicable to low-temperature work.

If the emf of a thermocouple is observed at three temperatures, about −70, −140, and −190 °C, the deviation curve can as a rule be drawn so as not to be in error at intermediate temperatures, in the range 0 to −190 °C, by as much as 2 microvolts. The relation

$$E = at + bt^2 + ct^3$$

with constants calculated from observed emfs at the foregoing temperatures, will give results almost as accurate; but the method of using Table 1, together with a deviation curve, is to be preferred both because it is more convenient and also because any serious error of calibration is strikingly evident as an irregularity in the deviation curve.

If a thermocouple is to be used only in the range 0 to −90 °C and an accuracy of ±2 microvolts is sufficient, a single calibration in subliming carbon dioxide is adequate. The deviation curve in this case is, of course, a straight line through the observed point and the origin. For most thermocouples a calibration accurate to ±2 microvolts is all that is justified, because inhomogeneities in the wires are likely to introduce larger errors.

If the thermocouple is calibrated at the oxygen boiling point as well as at the CO_2 point, a temperature-emf relation having a maximum error of less than 4 microvolts at temperatures between the CO_2 and oxygen points may be obtained. The deviation curve should approximate a parabola, having its greatest curvature at the low-temperature end. If the deviation curve is found to be nearly linear the maximum error will be considerably less than 4 microvolts. Wiebe and Brevoort[12] state that the deviation curve for a copper-constantan thermocouple calibrated at these two temperatures can be represented by the quadratic equation

$$\text{Deviation} = aE + bE^2$$

with an accuracy of about 0.05 °C (0.8 to 2.0 μv). Adams' table was used as the basis of reference. They base their conclusion on calibrations of seven thermocouples of their own and one from another laboratory. Their somewhat smaller limit of error may probably be explained by the fact that the constantan of their thermocouples was not obtained from as great a number of sources as that of the thermocouples sent to this laboratory for calibration; hence they did not find quite as great a variation in the shapes of the deviation curves.

A thermocouple used only at low temperatures should be expected to maintain its calibration better than one subjected to temperatures which accelerate physical and chemical changes in the metals. Giauque and Egan[13] and Stephenson and Giauque[14] checked some copper-constantan thermocouples several years after their original calibration. They found some discrepancies at temperatures between −190 and −260 °C, but above −190 °C no change in calibration of as much as 0.05 °C was found. Aston[15] reports a somewhat similar experience, with evidence that the changes observed at very low temperatures were due to repeated cooling of the thermocouples. His results also indicate that, at temperatures above −200 °C, a copper-constantan thermocouple will not change its calibration by more than 0.05 °C over a period of several years.

Summary

Thermocouples sent to the National Bureau of Standards for calibration at low temperatures are compared with a standard platinum resistance thermometer in a bath of uniform and constant temperature. The emf-temperature relation over an extended range is obtained by measuring the emf at a few selected temperatures and plotting the deviations from the values in a standard table. Deviation curves of a number of copper-constantan thermocouples from different sources indicate that, if the demand for accuracy is not too exacting, two points, the CO_2 sublimation temperature and the oxygen boiling point, may be used to obtain a calibration covering the range 0 to −190 °C. Thus a fair calibration may be obtained even though a platinum resistance thermometer and its accessory apparatus are not available. Furthermore, the apparatus used to attain the fixed temperature is not complicated. This is particularly true of the apparatus and material required for the CO_2 point. Ordinary commercial solid carbon dioxide is used, and the apparatus consists of a Dewar flask, an electrical heating coil, and a barometer for determining the pressure. This calibration at the temperature of subliming CO_2 is sufficient to establish the temperature-emf relation from 0 °C to −90 °C with an accuracy of ± microvolts. It should be remembered that unless considerable care is taken in selecting the constantan wire, errors due to inhomogeneity may be larger than errors of observation. Thus the quality of the thermocouples may not justify the highest accuracy of calibration, and the simpler method of using one or two fixed points may be entirely adequate.

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The Use of Copper-Constantan Thermocouples For Measurement of Low Temperatures Particularly in Calorimetry

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The Pennsylvania State College

Introduction

The copper-constantan thermocouple serves as a convenient and reasonably accurate means of determining temperatures down to liquid air temperatures (85 °K). With precautions it can be used down to as low as 11 °K. However, partly because of decreased sensitivity and partly because of changes in calibration, the instrument is not as suitable for precision work below 85 °K as it is above. The effect of sensitivity on precision is shown in Table 1, which is a condensed electromotive force-temperature conversion table for a standard copper-constantan thermocouple. The dT/dE values at 12 °K are over five times as large as they are at 100 °K, *i.e.*, the sensitivity is one-fifth as great. At this temperature 0.01 °K is equivalent to only 0.03 microvolt out of a total reading of 6100 μV. To get this precision with a single element requires a constancy of one unit in the fifth decimal place of the standard cell and all the attendant difficulties in maintenance.

Table 1. Condensed Table for Copper-Constantan Thermocouple S-6 (Cold Junction in Ice) 273.16 °K = 0 °C.

Reading of Couple (microvolts)	Temperature (°C)	Temperature (°K)	Derivative $\frac{dT}{dE}$ (degrees/microvolt)
− 1000	+ 25.38	298.52	0.0247
0	0.00	273.16	0.0263
1000	− 27.16	246.00	0.0282
2000	− 56.53	216.63	0.0307
3000	− 88.99	184.17	0.0345
4000	− 126.20	146.96	0.0407
4500	− 147.62	125.54	0.0455
5000	− 172.01	101.15	0.0528
5500	− 201.27	71.87	0.0662
6000	− 243.52	29.64	0.125
6100	− 260.74	12.42	0.284

Construction of Thermocouples

When the thermocouples are to be soldered to a metal surface, as they are in calorimetry, they are limited to a single element. It is best to use at least three parallel constantan wires (No. 30 B. & S. double-silk-insulated) and a single No. 36 B. & S. copper wire.[1]

The parallel wires tend to cancel out the effect of inhomogeneifies. The wires are conveniently wrapped together with silk thread as shown in Fig. 1.

The connection to the potentiometer is best made by soldering the cold and hot parts of the copper wire to two thin copper strips held between Bakelite plates. The terminals thus formed are seen in Fig. 1. (The serial number, S-5, is marked on the Bakelite).

Method of Calibrating Thermocouples

The most convenient way of obtaining a series of standard thermocouples is to compare the constantan wires and the copper wires separately against those of a master thermocouple which is calibrated later against a gas thermometer. If they are to be used in calorimetry the thermocouples to be compared should be fastened to a metal block (best of lead) similar to the calorimeter, whose temperature is attained and maintained in the same way as that of the calorimeter. The thermocouples should be located in the same way as they are to be in the calorimeter. Only in this way can the effect of inhomogeneities in the temperature gradient be effectively minimized.

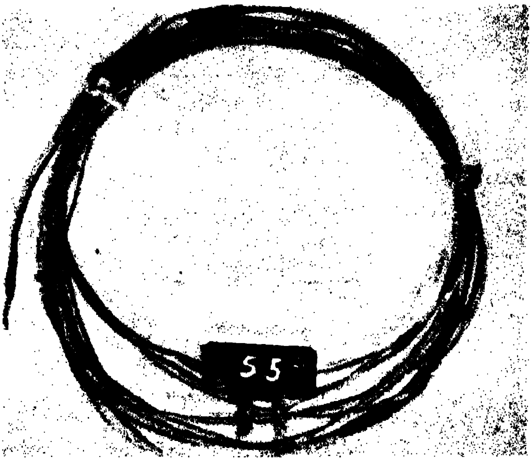
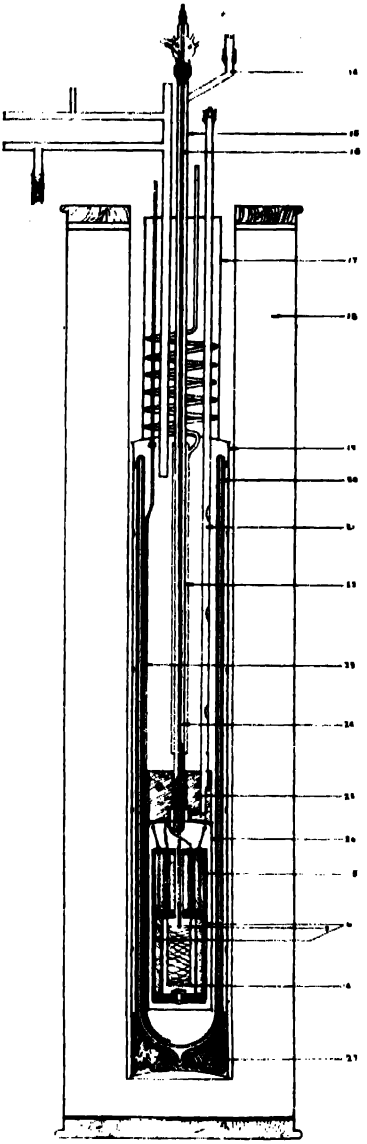


FIG. 1. A copper-constantan thermocouple for calorimetry.

In the investigation at The Pennsylvania State College Cryogenic Laboratory, nine thermocouples, S-1 to S-9, were compared in this way. Eight of these have five parallel constantan wires while S-9 has only three. No significant difference between S-9 and the other thermocouples has been noted. The apparatus used was similar to the calorimeter shown in Fig. 2, except that a lead block replaced the calorimeter. To this block were fastened the nine thermocouples.

The gas thermometer against which the master thermocouple is compared should also follow the design of the calorimeter as far as possible, and the thermocouple should have its temperature gradients located as they are to be when it is used with the calorimeter. Fig. 3 is a schematic drawing of the helium thermometer used for this purpose. It closely resembles the hydrogen thermometer used by Giauque, Buffington and Schultze.[1]

This figure should be compared with Fig. 2, which is a drawing of one of the calorimeter assemblies with which the thermocouples were to be used. The thermocouples are fastened to the bottom of the copper thermometer case just as they were fastened to the bottom of the calorimeter. A section of the thermocouple is wrapped around the calorimeter and a section passes through the radiation shield. The same section of each thermocouple was disposed of in the same way in the comparison apparatus and in the gas thermometer. The gas thermometer case and the junction of the thermocouple soldered to its bottom could be kept at constant



- 3, 4. Thermocouple wells with standard thermocouples in place on top and bottom of calorimeter.
- 5. Radiation shield.
- 6. Polished aluminum sheet on inside and outside of radiation shield.
- 14. Connection of cryostat can to high vacuum.
- 15. Cryostat tube.
- 16. Calorimeter filling tube wrapped with heater.
- 17. Liquid air cup.
- 18. Outer Kapok insulating case (147 cm long).
- 19. Monel Dewar case.
- 20. "Pyrex" glass Dewar.
- 21. Tube for introducing refrigerants.
- 22. Cryostat tube jacket.
- 23. Siphon tube to bottom of Dewar.
- 24. Thermocouples; current and potential leads to calorimeter.
- 25. Outer lead block.
- 26. Cryostat can.
- 27. Balsawood Dewar support.

FIG. 2. Low-temperature calorimeter. (Patterned after those of Giauque and collaborators.)

Scale: length of outer case 18 = 147 cm overall.

temperature by the high vacuum and the surrounding radiation shield. To guard against distortion of the 126-cc "Pyrex" thermometer bulb, as well as against diffusion of helium, the pressure in the thermometer case was kept equal to that within the bulb. The connection to the precision manometer was made with 0.5-mm capillary tubing. The "dead" space corrections and those for gas imperfection were made in the customary manner. From the results the electromotive force-temperature reference table was constructed.

Results of the Calibration of Thermocouples

Fig. 4 is a graph showing the deviations (Δ) of the temperatures, calculated from the microvolt readings of S-6 using the final reference table, (T_E), from

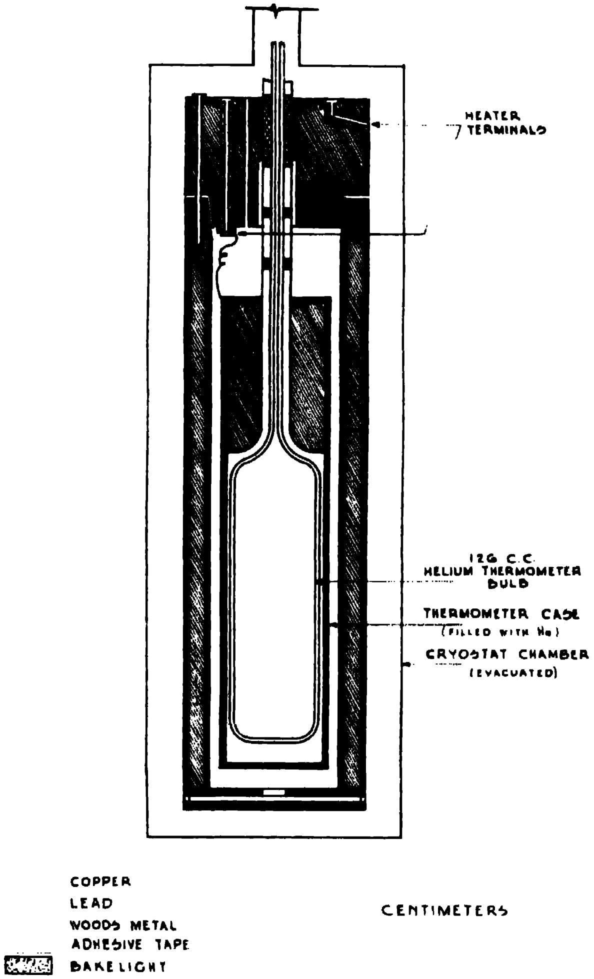

HEATER TERMINALS
126 C.C. HELIUM THERMOMETER BULB
THERMOMETER CASE (FILLED WITH He)
CRYOSTAT CHAMBER (EVACUATED)
COPPER
LEAD
WOODS METAL
ADHESIVE TAPE
BAKELIGHT
CENTIMETERS

FIG. 3. Helium Thermometer.

those observed with the helium thermometer (T_G), $(\Delta = T_E - T_G)$, over the range 12 to 273 °K.[2]

The maximum deviation is 0.06 °K occurring in one of the points at 40 °K.

The results of the comparison of the individual thermocouples with S-5 in two cases are shown graphically in Fig. 5.

The abscissa is the total electromotive force of S-5. The ordinates represent the electromotive force of S-5 minus that of S-6 in the upper graph and that of S-5

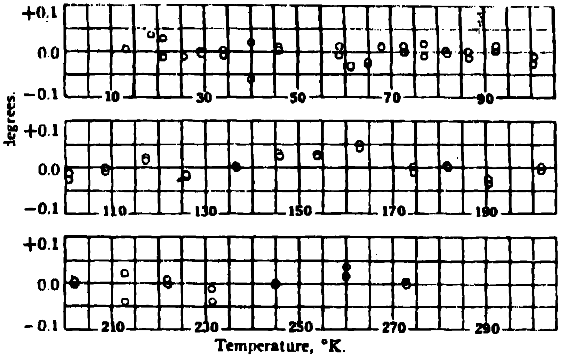


FIG. 4. Deviation plot for gas thermometer, comparisons of May 1-10, 1934.

minus S-4 in the lower. The dotted lines represent the difference in microvolts corresponding to 0.01° from the solid curve. It can be seen that except below 90 °K the precision of comparison is of the order of 0.01°. Near 20 °K the precision is of the order of 0.05°. The larger deviation of the points during a preliminary liquid hydrogen run may be an indication of changes produced by cooling. Such changes will be discussed presently.

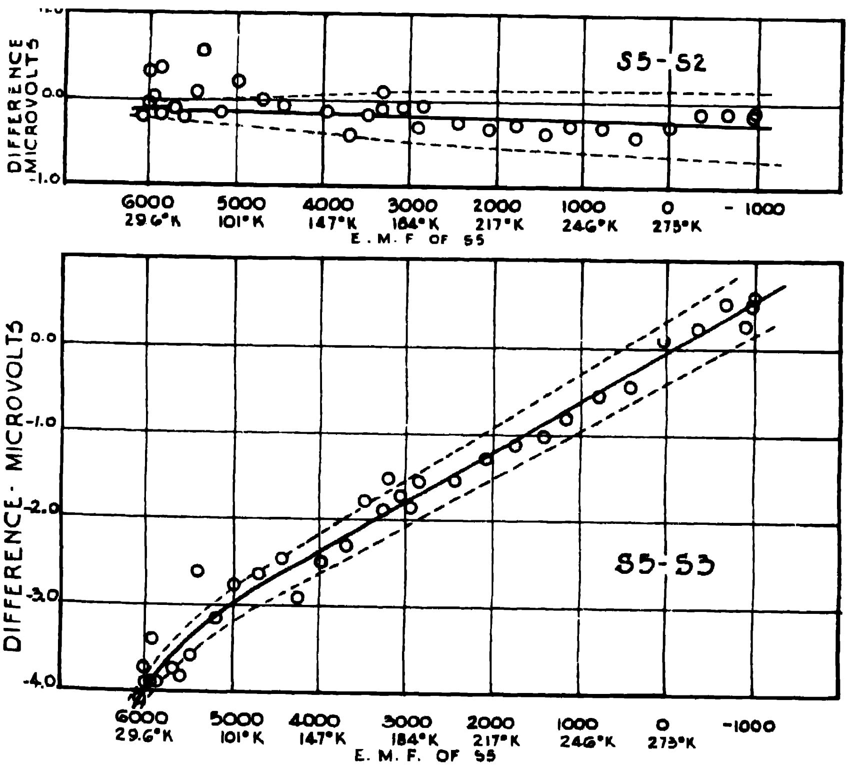


FIG. 5. Comparison of Thermocouples S-2 and S-3 with S-5.

The graphs, together with those for the other thermocouples, show that the microvolt deviation is practically proportional to the total microvolt reading down to 90 °K (5000 μ V.). Thus a copper-constantan thermocouple made from constantan wire which gives an electromotive force, at liquid air temperatures, within fifty microvolts of a reference table can be calibrated in a simple and accurate manner, if the constantan wire is from the same spool as that of the couple to which the reference table applies. The deviation from the table in microvolts is secured by taking a reading in boiling oxygen. The microvolt differences of the couple from the table will be proportional to the total microvolt readings of the thermocouple and can be secured from the single measurement. This assumption of proportionality should not produce errors greater than 0.05 °K. If the thermocouple differed from the table by 200 μ V. this method of calibration could scarcely produce an error greater than 0.3 °K. This subject is discussed elsewhere in the Symposium by R. B. Scott (The Calibration of Thermocouples at Low Temperature, page 206).

The Vapor Pressures of Hydrogen and Oxygen

Tables 2 and 3 show the results of oxygen and hydrogen vapor-pressure determinations using the final temperature scale. These vapor-pressure determinations are readily made by condensing the gas in the calorimeter depicted in Fig. 3. The temperature of the calorimeter (now the vapor-pressure bulb) can be main-

Table 2. Comparison of Copper-Constantan Thermocouple S-2
With Hydrogen Vapor Pressures, Mar. 28, 1935.
0 °C = 273.16 °K

T_1 obs. (°K)	Pressure (obs.) International (mm)	T_2 (calc.) (°K)	$\Delta T = T_1 - T_2$ (obs. − calc.)
18.00	343.2	17.95	+.05
19.90	650.5	19.85	+.05
20.23	720.7	20.19	+.04
20.63	813.9	20.59	+.04

T_1—calculated from microvolt reading on S-2 and tables.

T_2—calculated from equations of Keesom, Bijl and van der Horst (Leiden, 1931). Assuming 50% *ortho*, 50% *para* hydrogen.

normal hydrogen: $t = -260.865 + 1.0619 \log_{10} p_{mm} + 1.7233 \log_{10}^2 p_{mm}$

para hydrogen: $t = -260.937 + 1.0270 \log_{10} p_{mm} + 1.7303 \log_{10}^2 p_{mm}$

Table 3. Comparison of Copper-Constantan Thermocouple S-2
With Oxygen Vapor Pressures, April 1935.
0 °C = 273.16 °K

Date April 1935	T_1 obs. (°K)	T_2 calc., (°K)	$\Delta T = T_1 - T_2$ (obs. − calc.)
19	63.05	63.01	+.04
19	67.46	67.39	+.07
15	71.20	71.14	+.06
17	73.34	73.29	+.05
17	80.01	79.95	+.06
17	85.69	85.64	+.05
17	90.03	89.97	+.06

T_1—calculated from microvolt reading on S-2 and tables.

T_2—calculated from equation of Cath (Leiden, 1918).

$$\log_{10} p_{atm} = -(419.31/T) + 5.2365 - 0.00648T$$

with a correction for $\alpha_A \left(\frac{273.16}{273.09}\right)$

tained to within 0.01 °K for thirty minutes by the high vacuum and the radiation shield surrounding it which is kept at the same temperature. A precision manometer is attached to the filling tube and read by a cathetometer equipped with two telescopes possessing micrometer eye-pieces. The results for hydrogen are tabulated in Table 2, as the difference, $\Delta T = T_1 - T_2$. The temperature, T_1, is calculated from the microvolt reading of S-2 and the final reference table obtained for it. The temperature, T_2, is calculated from the vapor-pressure equations expressing the results of Keesom, Bijl, and van der Horst.[3a]

It should be pointed out that other investigators have observed similar positive deviations from the equation of Keesom, Bijl, and van der Horst, which are probably due to the vapor-pressure bulb of these authors being hotter than their thermometer. Thus our temperature scale yielded values of the normal boiling point of hydrogen in agreement with the most recent results.[3b] This is to be attributed to direct attachment of the thermocouple to the vapor-pressure bulb (calorimeter). A comparison with oxygen vapor pressures shown in Table 3 yielded almost identical deviations from the Leiden results[4] presumably for the same reason.

It is to be noted that more recent determinations[3b] of the boiling point of oxygen are in excellent agreement with those recorded here.

Changes in Calibration of Thermocouples

More than three years later the temperature indications of S-4 and S-7 were compared with those deduced from comparison with the helium thermometer in May, 1934. The comparison was made with the aid of fixed points. The values used for the oxygen and hydrogen vapor pressures were those on our original scale. Otherwise the best available data were used. The results are summarized in Table 4. No sensible change in calibration of these two thermocouples is evident from these results.

Table 4. Deviation of Temperature Indications of Copper-Constantan Thermocouples S-4 and S-7 from Those Deduced from the Helium Thermometer Comparison of May, 1934.

Date 1938	Average Temp. (°K)	S-4		Notes
		Average $\Delta T = T_1 - T_2$	Average $\Delta T = T_1 - T_2$	
Dec. 17	13.96	-0.19	-0.09	Hydrogen Triple Point 4th cooling to liquid hydrogen temperatures
Dec.	16.89	-0.07	+0.02	Hydrogen Vapor Pressure 4th cooling to liquid hydrogen temperatures
Dec.	18.47	-0.02	+0.05	
Dec.	20.29	+0.02	+0.11	
Nov. 26	43.77	0.00	+0.02	Upper Transition of Oxygen after 3rd cooling to liquid hydrogen temperatures
Nov. 26	54.34	0.00	-0.01	Triple Point of Oxygen after 3rd cooling to liquid hydrogen temperatures
Dec. 3	69.85	0.00	+0.02	Oxygen Vapor Pressures after 3rd cooling to liquid hydrogen temperatures.
Dec. 3	90.96	-0.03	-0.01	

T_1—calculated from microvolt reading on S-4 or S-7 and the reference table.

T_2—Temperature of fixed point. In the case of oxygen and hydrogen vapor pressures the value on our original scale was used. The other fixed points used were: triple point of hydrogen 13.96 °K (see reference 3b); upper transition point of oxygen 43.77 °K and triple point 54.34 °K [Giauque and Johnston, *J. Am. Chem. Soc.*, **51**, 2300 (1929)].

On the other hand S-2, after several coolings to liquid hydrogen temperatures, was found to have changed its calibration. The changes ranged from −0.49 at the triple point of hydrogen to −0.05 at the boiling point of oxygen, as can be seen from Table 5, which corresponds to Table 4. These results were obtained only two years after the first vapor-pressure comparisons.

Table 5. Deviation of Temperature Indications of Copper-Constantan Thermocouple S-2 from Those Deduced from Helium Thermometer Comparisons of May 1934, after a Total of Seven Coolings to Liquid Hydrogen Temperatures.

Date	Average Temp. (°K)	Average $\Delta T = T_1 - T_2$	Notes
Oct. 23, 1937	13.96	−0.49	Hydrogen Triple Point
Oct. 23, 1937	19.22	−0.34	Hydrogen Vapor Pressures
Oct. 23, 1937	20.3	−0.29	
Oct. 30, 1937	43.77	−0.07	Upper transition of oxygen
Oct. 30, 1937	54.34	−0.05	Oxygen Triple Point
Nov. 1936	64.83	−0.04	Oxygen Vapor Pressures
Nov. 1936	83.90	−0.05	
Oct. 30, 1937	68.90	−0.10	Oxygen Vapor Pressures

T_1—calculated from microvolt reading on S-2.
T_2—Temperature of fixed point. In the case of oxygen and hydrogen vapor pressures the value on our original scale was used. For other fixed points see foot of Table 4.

The changes which can occur on successive coolings to liquid hydrogen temperatures are shown in Table 6, in which changes of calibration of thermocouple S-9 are shown. These changes were noted when the thermocouple was put into use four years after its original calibration. The results seem to indicate that the successive coolings to liquid hydrogen temperatures are responsible for the changes in calibration. This is consistent with the fact that S-4 and S-7 showed no changes on the first cooling to liquid hydrogen temperatures three years after their original comparison against oxygen and hydrogen vapor pressures. No further observations on S-2 were possible due to its destruction by fire.

Table 6. Deviation of Temperature Indications of Copper-Constantan Thermocouple S-9 in 1938 from Those Deduced from the Helium Thermometer Comparisons of May 1934

	Average deviations $\Delta T = T_1 - T_2$			
Average Temp. (°K)	After 3rd cooling to Liquid H_2 temp.	After 4th cooling to Liquid H_2 temp.	After 5th cooling to liquid H_2 temp.	After 6th cooling to Liquid H_2 temp.
13.96		−0.31	−0.52	
19.57		−0.19	−0.31	−0.33
20.73		−0.18	−0.30	−0.29
43.77	−0.05			
54.34	−0.05			
60.70	−0.07			
70.90	−0.05			

T_1—Calculated from microvolt reading on S-9.
T_2—Temperature of fixed point. In the case of oxygen and hydrogen vapor pressures the value on our original scale was used. For other fixed points see foot of Table 4.

Stephenson and Giauque[5] have published the deviations of thermocouple W some ten years after its calibration at Berkeley by Giauque, Buffington, and Schulze. The deviations, shown in Table 7, are about one-half those eventually observed with S-2. No particulars concerning the treatment of the thermocouple in the interim are recorded. It is interesting that a section of the constantan wire used for the

Berkeley thermocouples gave about half the readings of an equal length of ours when it was drawn through liquid air and the emf was taken across the ends, and that the differences between individual couples were about half those between ours.

Table 7. Deviations of Copper-Constantan Thermocouple W of the Berkeley Cryogenic Laboratory.
0 °C = 273.10 °K

Temperature (°K)	$\Delta T = T_1 - T_2$	Notes
13.96	−0.17	Hydrogen triple point
20.37	−0.15	Hydrogen boiling point
43.76	−0.13	Upper transition point of oxygen
54.39	−0.11	Melting point of oxygen
90.13	−0.01	Boiling point of oxygen

T_1—Calculated from microvolt reading of thermocouple W and Berkeley Tables [Stephensen and Giauque, *J. Chem. Phys.*, **5**, 149 (1937)].
T_2—Temperature of the fixed point.

A consideration of the changes observed with S-2 and the results shown in Tables 6 and 7 indicate that above 90 °K the copper-constantan thermocouple may be used as a permanent standard to within about 0.05 °K; below that it requires frequent checking. In the liquid hydrogen region the changes may reach about 0.5 °. However these changes can be incorporated into the deviation plot for the thermocouple; the resulting error is then probably not greater than 0.05 °K, inasmuch as all deviation curves have the same shape and there is no difficulty in drawing the new deviation curve. It will be seen that such an error does not effect the accuracy of heat capacity or entropy measurements obtained with the thermocouple to within their accuracy of 0.1 per cent. This is because such small changes do not affect the derivative of the thermocouple appreciably and therefore are without effect on C_p; and because, down to 50 °K, 0.05 °K causes but 0.1 per cent error in T, and hence in C_p/T. Below 50 °K, the accuracy of the heat-capacity measurements, as limited by other factors, does not justify any higher accuracy in the entropy than given by 0.05 °K accuracy in the absolute temperature.

Acknowledgment

For much of the data in this paper the author is indebted to Dr. Eugene Willihnganz, Dr. George H. Messerly, and Dr. Maxwell L. Eidinoff.

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Liquid-In-Glass Thermometers

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I. Introduction

The mercury-in-glass thermometer as an instrument of precision attained its highest development some fifty years ago. The thermometers used and distributed at that time by the International Bureau of Weights and Measures represented a grade of workmanship which it is not worth while to attempt today, when higher precision than is possible with mercury-in-glass thermometers can be attained easily with electrical thermometers.

These early high-precision thermometers were designated "primary standards," although the term is rather a misnomer. The idea underlying the use of the term was that the instrument was "fundamental bestimmbar, streng in sich calibrirbar," that is, by means of a calibration with mercury threads, and observation of the readings at 0 °C and 100 °C only, a reproducible scale could be established. To make the scale precise, it was necessary to take account also of the effects of pressure, both internal and external, and of the effects of changes in bulb volume, usually referred to as changes in the zero reading, or the thermometer zero. The calibration with mercury threads was exceedingly laborious, but if the thermometer survived it, and most of them did, any thermometer could be used to set up a more or less reproducible mercury-in-glass scale. The scale was strictly reproducible only if the composition of the glass was the same in all the thermometers. A considerable degree of success was attained for some time in maintaining a constant composition, until more lead was added to improve the workability of the glass.

The mercury-in-glass scale was of little value until data became available for reducing from that scale to the gas thermometer scale, or in modern times, to the thermodynamic scale. These data were supplied by the monumental work of Chappuis,[1] who compared eight calibrated thermometers made of French hard glass with a hydrogen gas thermometer. The gas thermometry of Chappuis seems to have involved some superstitions; thus, the bulb had a volume of one liter, its length was a little over one meter, and some special significance appears to have been attached to an initial (ice point) pressure of 1 meter of mercury. However, the work of Chappuis is one of the outstanding examples of precise gas thermometry.

The scale distributed by the International Bureau by means of "primary standard" mercury-in-glass thermometers was known as the "International Hydrogen Scale," and it occupied an important position for some twenty years. The scale actually was extended to cover the range from −35 to +200 °C, but only the part between 0 and 100 °C ever received general acceptance. The theory and the technique of using these thermometers is fully covered in the paper by Chappuis, supplemented by Guillaume's book.[2] Both of these works are still useful sources of information for any one interested in the technique of precise thermometry, even though the basic ideas are now obsolete.

The characteristics that made high precision so difficult to attain with the primary standard thermometers are still present in the thermometers in use today, and furnish an adequate reason for the numerous precautions that must be taken to obtain satisfactory results. Although liquid-in-glass thermometers are no longer used for measurements of the highest precision, they are useful, and in fact indispensable, laboratory and plant tools for making a great variety of temperature measurements. They comprise a convenient and relatively, inexpensive series of instruments for use in the range −190 to 500 °C, or somewhat higher, in a large number of processes for which a ready and convenient method of temperature measurement is important. The boundaries of this interval are determined at the lower end by the availability of suitable liquids, and at the upper end by the softening ranges of thermometric glasses, though recently thermometers usable as high as 600 °C, or somewhat higher, have appeared on the market. This paper discusses the types of liquid-in-glass thermometers generally available and the performance which may be expected from such instruments.

Other temperature-measuring instruments available for use in this range include resistance thermometers and certain kinds of thermocouples. These instruments, with the necessary indicating accessories, furnish additional and accurate methods of temperature measurement. They are, in general, more expensive and somewhat more cumbersome.

Self-contained or long-distance recording and indicating thermometers using liquid, gas, vapor pressure or bimetallic units for the actuating elements also form a useful group for temperature measurement over this range,. but they are not in the scope of this paper.

II. The Temperature Scale

"The Thermodynamic Centigrade Scale, on which the temperature of melting ice, and the temperature of condensing water vapor, both under the pressure of one standard atmosphere, are numbered 0° and 100°, respectively, is recognized as the fundamental scale to which all temperature measurements should ultimately be referable." [3]

The practical temperature scale in general use is the International Temperature Scale adopted in 1927 by the General Conference of Weights and Measures.[3] This "scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated according to a specified procedure at the fixed temperatures." On this scale, temperatures in the interval 0 to 660 °C are defined in terms of the resistance of a standard form of platinum resistance thermometer calibrated at 0 °C, 100 °C and the boiling point of sulfur (444.60 °C). Temperatures below 0 °C are also defined in terms of such a standard, using an additional calibration at the boiling point of oxygen (−182.97 °C). Since the indications of various standard resistance thermometers differ from one another by less than the experimental errors of gas thermometry, the standard scale defined by reference to the platinum resistance thermometer is more reproducible than the scale defined by the gas thermometer, but may differ from the thermodynamic scale by the amount of the error in the gas thermometric measurements upon which the standard scale is based. A concise history of the temperature scale is given in a paper by Waidner, Mueller and Foote.[4]

The International Hydrogen Scale was made available to the National Bureau of Standards by means of a number of mercury-in-glass (*verre dur*) thermometers which had been standardized according to the ritual prescribed for such work by the International Bureau of Weights and Measures. The reproducibility of the scale was thoroughly investigated by Waidner and Dickinson[5] in 1907. Shortly after this investigation was completed, resistance thermometers standardized essentially according to the procedure now specified for the International Temperature Scale were also used as standards. During this transition period, both the mercury-in-glass thermometers and the resistance thermometer were used as standards, and many comparisons between the two were made in the course of routine testing. In general, the result of the comparisons showed that if there was any real difference between the two scales, it was smaller than the accidental errors of the individual comparisons. The results of these surveys were never published by the National Bureau of Standards. A systematic survey was made later by Hall[6] whose conclusions were:

"It was found that the change from certain Tonnelot * and Baudin † thermometers to the platinum thermometer as a means of interpolation between 0 °C and 100 °C will not alter the temperature scale of the National Physical Laboratory in that range by more than 0.002 °C between 0 °C and 50 °C or 0.005 °C between 50 °C and 100 °C.

"No difference between the thermodynamic scale and the scale defined by the platinum thermometer was detected, the mercury in verre dur thermometers being used as an intermediary."

All liquid-in-glass thermometer tests made by the National Bureau of Standards are referred to the International Temperature Scale, defined, in this range, in terms of the resistance of the standard platinum resistance thermometer.

III. Notes on Liquid-In-Glass Thermometers

The usual type of mercury-in-glass thermometer for use below about 200 °C made in this country, is made of two kinds of glass; the bulb being made of the grade of thermometric glass suitable for use over the range in which the thermometer is intended for use, and the stem of one of the more workable stem glasses, having a white or colored backing, or some other arrangement, as an aid to reading. For thermometers intended for use at higher temperatures, and in most of the foreign product, the entire thermometer is made from the same piece of thermometric tubing, the bulb being fashioned directly in the end.

Thermometers of the type just described depend for their indications primarily upon the relative expansion of mercury, or other liquid, in glass. Since the ratio of the volume of the bulb to the volume of the bore is large in most cases, only the changes in the volume of the bulb need, in general, to be considered. Volume changes, in addition to the expansion of the glass with rising temperatures, occur, with time and use, in the glass of a finished thermometer; and these changes are, in general, of sufficient magnitude to affect the accuracy and must be considered in arriving at temperature values. These changes may be determined and accounted for by the determination of reference point readings from time to time.

The effect of changes in the glass on the indications of a thermometer is evident from the following: The bulb of a centigrade mercury-in-glass thermometer has a volume equivalent to about 6000 degrees of the scale. Therefore, if a change of one part in 6000 occurs in the bulb volume, the readings will be changed by about one degree. If the corrections are to remain constant to 0.05 °C, no change greater than 1 part in 100,000 must occur in the bulb volume. Similarly the bulb of a Fahrenheit mercury-in-glass thermometer has a volume equivalent to about 11,000 degrees of the scale, so that if the corrections are to remain constant within 0.1 °F, no change greater than 1 part in 100,000 must occur in the bulb volume. Changes of the order of 1 part in 100,000 may readily occur in the volumes of thermometer

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* Thermometers made by Tonnelot of Paris in the late 1800's.

† Thermometers made by Baudin of Paris about 1900.

bulbs, and if accuracies of the order of 0.05 °C or 0.1 °F are expected these changes must be determined and allowed for.

Since the volume of the bulb is large compared with the volume of the bore, changes in the volume of the latter will not affect the accuracy appreciably, unless such changes are proportionately very much larger than those in the bulb. It follows therefore, that if the reading at any point on the scale has changed since calibration, all other points will have changed by the same amount. The amount of the change can readily be determined by an observation at a reference point, and the change can be allowed for over the entire length of scale.

A. Reference Points. The ice point, 0 °C or 32 °F, is the most convenient reference point for use in determining the changes mentioned above. Other points, such as the steam point, or a point in the room temperature range (20 to 30 °C or 68 to 86 °F) may also be used. If a point in the room-temperature range is used, comparison must be made with a standardized thermometer which has an ice point on the scale.

B. Changes in Thermometers with Time and Use. Thermometer bulbs, whether used or not, are subject to progressive changes in volume. Such changes will not exceed 0.1 °C for good grades of thermometric glasses, provided the thermometer has not been heated above 150 °C. It is for this reason that the National Bureau of Standards will issue certificates showing corrections only to the nearest 0.1 °C or 0.2 °F for thermometers not graduated above 150 °C or 300 °F, which have no fixed point on the scale. When accuracies better than 0.1 °C are expected from such thermometers, reference point determinations must be made and corrections applied. Changes in the bulb volume of thermometers used at higher temperatures, up to 500 °C or 900 °F, cannot be predicted but may be expected to exceed the progressive changes mentioned above. Some of the glasses suitable for use at temperatures as high as 600 °C or 1100 °F appear to be subject to smaller changes in bulb volume than the borosilicate types used below 500 °C.

In the use of liquid-in-glass thermometers, reference-point readings serve to indicate and determine bulb volume changes. For centigrade thermometers not used above 400°, or Fahrenheit thermometers not used above 750°, all scale readings may be assumed to have changed by the same amount as the change in reference-point reading, that is, all readings will be higher or lower by the same amount that the reference point reads higher or lower since the calibration. This statement may not be strictly applicable to thermometers used at higher temperatures, such as 500 °C or 950 °F or above.

C. Temporary Changes in Bulb Volume. In addition to the more or less permanent changes in bulb volume described above, there are temporary changes resulting from heating, which may require consideration in thermometers graduated in 0.1- or 0.2-degree intervals, and not intended for use above 150 °C or 300 °F. If a thermometer which has been at room temperature for several days is heated to a higher temperature, the bulb will, within a few minutes, assume the volume corresponding to the higher temperature. If the bulb is then cooled to the original temperature, it does not at once return to the original volume but remains somewhat larger, with a consequent "depression" in reading. For good grades of thermometric glasses this depression is somewhat less than 0.01 degree for each 10 °C that the bulb is heated above the original temperature. This depression is fairly regular if the thermometer is not heated above 150 °C, and disappears almost entirely in a few days. Above 150 °C the changes become somewhat erratic and cannot be predicted.

It is evident from the above that these changes are of sufficient size to require attention in accurate temperature measurement. Since, at the National Bureau of Standards, thermometers, except certain types designed for differential measurements, are tested beginning at the lowest temperature and working up, the error resulting from the temporary depression can be avoided by using them in the same way, that is, by measuring the lowest temperature to be determined first and the higher temperatures in succession. It should be noted in this connection that if thermometers are read to the nearest 0.01 or 0.02 degree, the depression error may readily exceed the error in reading.

Table 1. Values of Ice Point Depression for Certain Types of Thermometric Glasses.[7]

Glass	Ice Point Depression for 100 °C
Verre dur	0.07 to 0.11
Normal types	0.04 to 0.08
Borosilicate types	0.03 to 0.04
Jena 1565^{III}	0.01
Jena Combustion	0.03

The ice point depression is the difference between the ice point reading of the thermometer taken after it has been for some time at a constant temperature and the ice point reading taken immediately after the thermometer has been for a sufficiently long time—some minutes or hours—at some higher temperature. For example, a thermometer which has been at room temperature for some time will read about 0.05 degree lower at 20 °C and about 0.01 degree lower at 60 °C after heating to 70 °C than it would have if it had been used successively at 20 and 60 °C without previous heating to 70 °C.

D. Changes in Bulb Volume Due to Annealing. Another change to which the indications of a thermometer are subject is the annealing change at high temperatures.[8,9] If the glass has not been properly annealed, it will progressively contract when exposed to relatively high temperatures, 300 °C or 600 °F or above, causing the indications of the thermometer to rise progressively. For the glasses from which thermometers for use up to 450 °C or 850 °F are made, these changes may be as much as 20 °C or 35 °F if the instruments have not been properly annealed. For well-annealed thermometers, not subjected to excessive temperatures, these changes are small and can readily be allowed for by initial and subsequent determinations of the reference-point reading and application of the necessary corrections. In the use of high-temperature thermometers care should be taken not to overheat them. When glass approaches its softening range the high internal pressure enlarges and permanently injures the bulb.

E. Upper Temperature Limits. The upper temperature limits to which the several thermometric glasses in general use may be safely heated are determined by the softening ranges of the glasses. Thermometers having bulbs made of Corning normal or Jena 16^{III} and stems of a more workable lead or flint glass can be safely used at temperatures up to 400 °C. If the entire thermometer is made of the normal type glass, 450 °C is a safe upper limit. Thermometers made of Corning borosilicate or Jena 59^{III} can be safely used for temperatures up to 500 °C or possibly as high as 520 °C for short periods of heating. For temperatures above 500 °C, Jena combustion tubing provides a glass safe for use up to 560 °C. Thermometers made of Jena 1565^{III} or Supremax glass can be safely used as high as 600 °C or somewhat higher.[7,10]

F. Thermometric Lag. The basic equation used in the mathematical treatment of thermometric lag is

$$\frac{dU}{dt} = -\frac{1}{\lambda}(U - U_0)$$

in which U represents the temperature of a thermometer, U_0 that of the medium in which the thermometer is immersed, t is the elapsed time and λ is a constant which depends upon the type of thermometer, the characteristics of the medium and the speed with which the medium moves relative to the thermometer. The usual treatment of the equation yields two useful results concerning the significance of the constant λ.

(1) If a thermometer at temperature U is in a medium at constant temperature, U_0, then λ represents the time required for the difference $U - U_0$ to be reduced to

$$\frac{1}{e}(U - U_0) = .37(U - U_0)^*$$

(2) If a thermometer is immersed in a medium, the temperature, U_0, of which is changing at a uniform rate, then after the temperature has been changing for a sufficiently long time, λ represents the interval between the time when the medium reaches any particular temperature and the time when the thermometer attains that temperature.

For most uses, the errors introduced by thermometric lag are of little importance. The lag of a liquid-in-glass thermometer is determined largely by the diameter of the bulb, and depends very little on the length of a cylindrical bulb. From time to time specifications appear in which the size of a thermometer bulb is specified and in addition a specification concerning lag is included. If the lag requirement is not inconsistent with the dimensions, no harm is done, but if this is not the case the manufacturer's only choice, if he undertakes the task, is to ignore one of the requirements.

Illustrative Values of λ[11]

Table 2. Values of λ for Some Types of Thermometers.

Type	Mercury-in-glass bulb Diameter (mm)	Mercury-in-glass bulb Length (mm)	Lag in well-stirred water (seconds)
Laboratory	4.5	25	2.1
Calorimetric	9.0	52	4.8
Beckmann	13.0	40	8.7
Beckmann—Large capillary above the bulb			50.0
Platinum Resistance Thermometer—Callendar type			15.5

Table 3. Values of λ for Several Velocities of Three Different Media.[11]

Small-bulb "Chemical" Thermometer. λ in Secs.

Velocity past bulb in cm/sec	0	1	5	10	50	100	500	1000	
Water	10.0	5.1	3.3	2.9	2.4	2.3			2.2 sec. (any medium)
Oil	40 to 50	13.4	7.5	6.4	4.8				
Air	190	170	148	128	71	58	33	25	

* $e^{-1} = \frac{1}{2.718} = 0.4$, approximately.

G. Effect of Pressure. It has already been mentioned that in using the old "primary standard" thermometers, it was necessary to take account of the effects of pressure, both internal and external. This is not surprising, since these thermometers were read to 0.001 °C, which corresponds to 1 part in 6,000,000 in the volume of the bulb, and obviously very little change in pressure is required to change the volume of the bulb by 1 part in 6,000,000.

If a thermometer bulb is subjected to an external hydrostatic pressure, the volume will decrease, the change being directly proportional to the diameter of a cylindrical bulb, and inversely proportional to the wall thickness. If the pressure change is internal, such as results from turning the thermometer from a horizontal to a vertical position, the increased pressure not only increases the volume of the bulb, but also compresses the contained mercury, so that the internal pressure coefficient is about 10 per cent greater than the external.

Experience with a large number of thermometers of different makes indicates that the pressure coefficient of a thermometer having a bulb diameter between 5 and 7 mm is of the order of 0.1 °C or 0.2 °F per atmosphere. Values of this order of magnitude have been found so consistently for numerous thermometers over a long period of years that the values may be used with considerable confidence for estimating the probable magnitude of pressure effects.

IV. General Characteristics of Liquid-in-Glass Thermometers

Liquid-in-glass thermometers include a general and varied group which may be classed as laboratory or "chemical" thermometers. These serve in some instances for definite purposes, but more often serve for general use. Other thermometers designed for special and definite uses are:

Beckmann
Calorimetric
Industrial
Clinical or medical

These special types, designed in each case for either total or partial immersion use, will be discussed separately after some general characteristics of thermometers have been considered.

Most of the thermometers made in this country, with the exception of the Beckmann, which follows the established design fairly closely, are of the etched-stem type, whereas those of foreign make include a large percentage of the enclosed scale (einschluss) type. Etched-stem thermometers have, in general, a smaller stem diameter than the enclosed-scale type, but because of the greater distance between the mercury column and the scale, parallax may more readily affect the readings of the etched-stem type. However, the scale and capillary of some forms of the enclosed-scale type may become displaced with respect to each other and thus introduce errors unless fiducial marks appear and are used. The computation of the correction for emergent stem is more unreliable for the enclosed-scale type by reason of the uncertainty as to the actual temperature inside the glass case.

Design, workmanship, and quality of material affect the performance of liquid-in-glass thermometers. Glasses suitable for thermometric bulbs and their behavior have been previously discussed. This section deals with other features which affect the performance of thermometers and which should be given attention in manufacture and use.

The readings of mercury-in-glass thermometers are arrived at by measuring the differential expansion of a relatively large quantity of mercury in the bulb by the travel of the end of a capillary thread of the mercury in the bore of a graduated stem. Obviously it appears desirable for ease in reading that this travel be as large as possible per degree. This can be accomplished either by increasing the size of the bulb or by decreasing the cross-section of the bore, that is, by increasing the length of a degree on the scale. These devices however are limited in practice on the one hand by bulb sizes which are practicable, and on the other by the smallest cross-section of the capillary through which a mercury thread will move uniformly. If the mercury and the glass are clean, that is, if the thermometer has been constructed according to good manufacturing practice, no appreciable sticking of the mercury column should occur if the diameter of a circular cross-section of the bore is at least of the order of 0.1 mm, though it should preferably be larger. For bores smaller than this in cross-sectional area erratic behavior of the mercury column may be expected. Elliptical or flattened bores are not to be recommended. It is evident from the above that increasing the length of a degree on the scale, for practicable bulb sizes, improves thermometric performance to a certain point only, beyond which the precision in reading graduation marks may readily be mistaken for accuracy in temperature measurement.

Other factors, such as ice-point changes, unless exactly accounted for, and differences in external pressure may account for inaccuracies many times greater than the precision in reading which the lines on a scale in 0.01- or 0.02-degree divisions may be capable of yielding. It is altogether desirable that graduation marks should be evenly spaced, should not be too wide and in general should show the qualities of good workmanship. However the mistaken concept that the ultimate limit of the precision in reading of distances between graduation marks on a glass stem determines the accuracy performance of the thermometer should be dispelled.

Graduations too close to an enlargement in the capillary or too close to the bulb may lead to appreciable errors. In general, no significant errors would result from the use of a thermometer on which the distances between the bulb and graduations and between enlargements in the bore and graduations are not less than the lengths listed below.

(1) A 13-mm length of unchanged capillary between the lowest graduation and the bulb, provided the graduation is not above 100 °C (212 °F).

(2) A 5-mm length of unchanged capillary between the last graduation below an enlargement and the enlargement.

(3) A 10-mm length of unchanged capillary between an enlargement and the graduation next above, if the graduation is below 100 °C (212 °F) or a 30-mm length if the graduation is above 100 °C (212 °F).

(4) A 10-mm length of unchanged capillary above the highest graduation, provided there is an expansion chamber at the top of the thermometer; a 30-mm length if there is no expansion chamber.

The width of graduation marks must be taken into account in reading. Graduations spaced too closely are difficult to read and may lead to error. Scales graduated in 1-, 0.5-, 0.2-, or 0.1-degree intervals or decimal multiples or submultiples thereof have been found satisfactory and avoid the confusion arising from attempting to read ¼-degree intervals.

The design of a thermometer should include a reference point on the scale when required. Thermometers not intended to give accuracies better than 0.1 °C or 0.2 °F and not intended for use above 150 °C or 300 °F, and thermometers intended for measurement of temperature differences only, need not include such a point on the scale. Where a reference point such as 0 °C or 100 °C appears on a thermometer scale, the graduations should extend a few divisions above and below such reference point. Thermometers, particularly those graduated above 300 °C or 600 °F should be adequately annealed, so that heating will not greatly change their indications. Such changes as do occur should be determined from time to time by reference-point readings.

Mercury-in-glass thermometers graduated for use above 100 °C should have the capillary above the mercury column filled with a dry inert gas, such as dry nitrogen, under pressure, to retard vaporization of the mercury. Gas filling for thermometers for use at lower temperatures is optional. The pressure required varies with the temperature and the construction of the thermometer, about one atmosphere being required at 300 °C, about four and a half atmospheres at 450 °C, and about 20 atmospheres at 550 °C.[8] For temperatures below 100 °C vaporization may be prevented by keeping the top of the mercury column cool.

Graduations extending higher on the scale than the temperature to which the thermometer may be heated safely are misleading and may be the cause of the bulb being permanently enlarged or entirely destroyed.

V. Total and Partial Immersion Thermometers

A. Total Immersion Thermometers. Some thermometers are pointed and graduated by the maker to read correct or nearly correct temperatures when the bulb and entire liquid index in the stem are exposed to the temperature to be measured, whereas other thermometers are so pointed and graduated that they will read correct or nearly correct temperatures when the bulb and a short length of the stem only are in the bath. Thermometers of the former class are known as "total immersion" and those of the latter class as "partial immersion" thermometers.

Total immersion thermometers are designed for complete immersion of all the mercury, but it is not necessary and in some cases not desirable that the portion of the stem above the meniscus be immersed. The heating of this portion to high temperatures might cause excessive gas pressures and consequent damage to the bulb.

In practice, a short length of the mercury column must be emergent from the bath so that the meniscus will be visible. The tendency toward vaporization at the meniscus is thus reduced, but not all the mercury column is at the temperature of the bath. If there is an appreciable temperature gradient near the top of the bath and if the temperature difference between the bath and its surroundings is large, the correction arising from these sources may be more important than is generally recognized, and may require attention, especially at bath temperatures above 150 °C. The correction may be determined by the same method of procedure as given in the following paragraphs.

If a liquid-in-glass thermometer designed and standardized for total immersion is used at partial immersion, that is, with a portion of the liquid column at a temperature different from that of the bath, the reading will be too low or too high, depending upon whether the surrounding temperature is lower or higher than that of the bath. For a total immersion thermometer so used, an "emergent stem correction" must be determined and applied in addition to the calibration corrections. This correction may be as large as 20 °C or 35 °F if the number of degrees emergent from the bath and the difference in temperature of the bath and the space above it are large.

The general formula used in computing the correction for emergent stem is:

$$\text{stem correction} = K \times n \ (T - t)$$

in which K = the differential expansion coefficient of mercury (or other liquid in the thermometer, such as alcohol, toluene, pentane, etc.) in the particular kind of glass of which the thermometer is made;

n = the number of degrees emergent from the bath;

T = the temperature of the bath;

t = average temperature of the liquid column of n degrees.

The value of t is to be determined by means of an auxiliary thermometer or thermometers, preferably with a capillary thermometer.[12]

The value of K depends on the coefficients of expansion of the glass and of the liquid and is a function of the temperature. Since, however, most of the change results from the varying coefficient of the mercury, the change in K with temperature for one glass may with some certainty be inferred from the change for some other glass. If the kind of glass from which the thermometer is made is not known, K may be taken to be 0.00016 for centigrade mercurial thermometers and 0.00009 for Fahrenheit thermometers. In many cases, in calculating emergent stem corrections for thermometers containing organic liquids, it is sufficient to use the approximate value of $K=0.001$. For purposes of computing the emergent stem correction the value of K may be considered as depending on the average of T and t, that is, $\frac{T+t}{2}$, and such values are shown in Table 8, reproduced from the "International Critical Tables." [7]

Example 1: Suppose an observed reading was 84.76 °C and the thermometer was immersed to the 20° mark on the scale, so that 65 degrees of the column projected into the air, and that the mean temperature of the emergent column was found to be 38°; then:

Stem correction = $0.00016 \times 65\ (85° - 38°) = +0.49$ °C.

The true temperature is therefore the observed reading, 84.76°, plus the tabular correction as interpolated from the certificate or report, plus the emergent stem correction (+0.49°).

Example 2: Suppose an observed reading was 780 °F and the thermometer was immersed to the 200° mark on the scale, so that 580 degrees of the column projected into the air, and that the mean temperature of the emergent column was found to be 170°; then:

Stem correction = $0.00009 \times 580\ (780° - 170°) = +32°$ as a first approximation.

Since the result shows that the bath temperature was approximately 780° + 32°, a second approximation should be made, using $T = 812°$ instead of $T = 780°$. This gives:

Stem correction = $0.00009 \times 580\ (812° - 170°) = +34°$.

The true temperature is therefore the observed reading, 780°, plus the tabular correction as interpolated from the certificate or report, plus the emergent stem correction (+34°).

It will be noted that if the average temperature of the stem is below that of the bulb, the sign of the correction will be plus, whereas if the temperature of the stem is above that of the bulb, the sign of the correction will be minus.

B. Partial Immersion Thermometers. "With the adoption of the platinum resistance thermometer for precision temperature measurements and the abandonment of mercury-in-glass thermometers as instruments of high precision there has been an increasing tendency to use partial immersion thermometers, graduated and standardized for definite depths of immersion, thus eliminating the necessity of determining and applying a correction for the emergent stem." [7]

Partial immersion thermometers made for 76-mm or 3-inch immersion for no specified stem temperature are available for general use. Partial immersion thermometers used in the industry for particular purposes are specified, designed and standardized for definite depths of immersion at stem temperatures prevailing during the test. Such practice has been furthered by technical organizations or societies, such as the American Society for Testing Materials, which assist in some of the problems of standardizing test methods in the industry. These methods of test contain specifications for some dozen or more partial immersion thermometers designed to be used in tests where the design of the apparatus requires short immersion lengths.

In some of these tests the method of use involves some departure from the usual supposed function of the thermometer, the departure being the circumstance that the thermometers need not, and in several cases do not, indicate temperatures, but that they must yield consistent values in repeat tests. To meet these requirements the tests must be reproducible, and in particular the stem temperatures must not vary by appreciable amounts. Such an arrangement requires definitely specified test methods, and thermometers identical, or nearly so, in design, standardized for stem temperatures prevailing in the test for which they were intended. Recently there has been some inclination toward measuring temperatures, and some of the thermometer specifications recently adopted have been designed with this criterion in mind. There exists a list of some thirty or more specifications for special design thermometers, copies of which are available from the A. S. T. M. Scrutiny of these lists may save time and expense in the selection of a suitable thermometer or in avoiding the necessity of creating additional types.

The scale error requirements for A. S. T. M. thermometers are smaller than those given in Tables 4 and 5, since the expectation is that the readings will be used without applying corrections, assuming these to be small enough to be negligible. Greater accuracy can be obtained with a thermometer showing appreciable corrections if the corrections are applied to the readings than with a thermometer showing smaller corrections which are not applied to the readings.

VI. Tolerances for Total and Partial Immersion Thermometers

Tables 4 and 5, reproduced from B. S. Circular No. 8, 4th edition, state the graduation intervals appropriate for the temperature ranges listed, the tolerances allowed by the National Bureau of Standards in issuing certificates, the accuracies which may be expected from the ranges and types represented and the decimal figure to which the corrections are stated on the document.

Under "graduation interval in degrees" are given the subdivisions suitable for thermometers of the ranges shown. The word "accuracy" used in these tables refers to the best values attainable in the use of the instrument when all the corrections are applied. Tolerance is the maximum error which may reasonably be allowed for a thermometer made in accordance with good manufacturing practice. In the thermometer trade and in some societies such as the American Society for Testing Materials the word "accuracy" is more generally used to indicate "scale error."

The final columns state the magnitude to which the corrections are given for thermometers tested by the National Bureau of Standards. They are stated to a somewhat higher order of accuracy than can be attained with certainty in testing the thermometer. This is done because it is preferable to give the corrections as found, since the result actually obtained is the best that can be deduced from any test, and considerable rounding off necessarily introduces an additional uncertainty.

Table 4. Tolerances for Total Immersion Mercurial Thermometers.[1]

Centigrade Thermometers

Temp. range in degrees	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometers for Low Temperatures				
−35 to 0	1 or 0.5	0.5	0.1 to 0.2	0.1
−35 to 0	.2	.4	.02 to .05	.02
Thermometers not Graduated above 150°				
0 up to 150	1 or 0.5	0.5	0.1 to 0.2	0.1
0 up to 150	.2	.4	.02 to .05	.02
0 up to 100	.1	.3	.01 to .03	.01
Thermometers not Graduated above 300°				
0 up to 100	1 or 0.5	0.5	0.1 to 0.2	0.1
Above 100 up to 300	1 or 0.5	1.0	.2 to .3	.1
0 up to 100	.2	.4	.02 to .05	.02
Above 100 up to 200	.2	.5	.05 to .1	.02
Thermometers Graduated above 300°				
0 up to 300	2	2	0.2 to 0.5	0.2
Above 300 up to 500	2	4	.5 to 1.0	.2
0 up to 300	1 or 0.5	2	.1 to .5	.1
Above 300 up to 500	1 or 0.5	4	.2 to .5	.1

Fahrenheit Thermometers

Temp. range in degrees	Graduation Interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometers for Low Temperatures				
−35 to 32	1 or 0.5	1	0.1 to 0.2	0.1
−35 to 32	.2	.5	.05	.02
Thermometers not Graduated above 300°				
32 up to 300	2	1	0.2 to 0.5	0.2
32 up to 300	1.0 or 0.5	1	.1 to .2	.1
32 up to 212	.2 or 0.1	.5	.02 to .05	.02
Thermometers not Graduated above 600°				
32 up to 212	2 or 1	1	0.2 to 0.5	0.2
Above 212 up to 600	2 or 1	2	.5	.2
Thermometers Graduated above 600°				
32 up to 600	5	4	0.5 to 1.0	0.5
Above 600 up to 950	5	7	1 to 2	.5
32 up to 600	2 or 1	3	.2 to 1.0	.2
Above 600 up to 950	2 or 1	6	.5 to 1.0	.2

A discussion of the relative accuracy of partial and total immersion thermometers is given by C. W. Waidner and E. F. Mueller,[14] and conclusions are quoted here: "The above considerations may be summarized in the statement that in all cases where the application of stem corrections is neglected, which includes a vast majority of routine laboratory temperature measurements, more accurate temperature measurements would be attained by the use of thermometers graduated as partial immersion thermometers; the same statement would apply for measurements at the higher temperatures (above 200 °C or thereabouts), even if stem corrections are applied, when the ordinary method of estimating average stem temperature is used instead of the more accurate capillary thermometer method. At the lower temperatures, on the other hand, a slight advantage rests with the

Table 5. Tolerances for Partial Immersion Mercurial Thermometers. [13]

Centigrade Thermometers

Temp. range in degrees	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometers for Low Temperatures				
-35 to 0	1 or 0.5	0.5	0.2 to 0.3	0.1
Thermometers not Graduated above 150°				
0 up to 150	1 or 0.5	1.0	0.1 to 0.5	
Thermometers not Graduated above 300°				
0 up to 100	1	1.0	0.1 to 0.3	0.1
Above 100 up to 300	1	1.5	.5 to 1.0	.2
Thermometers Graduated above 300°				
0 up to 300	2 or 1	2.5	0.5 to 1	0.5
Above 300 up to 500	2 or 1	5	1 to 2	.5

Fahrenheit Thermometers

Temp. range in degrees	Graduation Interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometers for Low Temperatures				
-35 to 32	1	1	0.3 to 0.5	0.1
Thermometers not Graduated above 300°				
32 up to 300	2 or 1	2	0.2 to 1.0	0.2
Thermometers not Graduated above 600°				
32 up to 212	2 or 1	2	0.2 to 0.5	0.2
Above 212 up to 600	2 or 1	3	1 to 2	.5
Thermometers Graduated above 600°				
32 up to 600	5 or 2	5.0	1 to 2	1
Above 600 up to 950	5 or 2	10	2 to 3	1

total immersion thermometer, if the stem correction is determined and applied in the usual manner, *i.e.*, by the intelligent use of an auxiliary thermometer to determine the average stem temperature. Thermometers graduated in intervals smaller than 0.5 °C should not, in general, be graduated as partial immersion thermometers, if the accuracy of which they are capable is desired, unless such finer graduation be deemed of sufficient importance solely from the standpoint of convenience in reading."

VII. Test Points

If it is the purpose of the test to determine the general quality of the thermometer, a few tests at random points on the scale will suffice. If it is the purpose of the test to determine corrections which are to be applied in the use of the thermometer, the points should be taken at intervals spaced so that intermediate corrections may be determined by interpolation with some degree of confidence. For this purpose test points need not be spaced closer than 40 divisions nor should they be farther apart than 100 divisions on a properly designed thermometer. The best values for use in interpolation are obtained if the test points include the points at which the scale value may change, that is, the pointing temperatures.

Requests for tests vary between two extremes, from those requested on the supposition that corrections may be confidently inferred over the entire length of scale from values obtained at say 0 and 500 °C, to those requested on the supposition that tests at 20° and 30° still leave a wholly unreliable value at 29°. The fallacy in such extremes is obvious.

Requests for thermometers having zero corrections at all points fail to take into account the fact that the labor involved in such precise pointing procedure would be wasted because of the changes in volume to which thermometer bulbs are known to be subject. Furthermore, a thermometer which has appreciable corrections will yield results just as accurate as one with small corrections, if the corrections are applied. A little consideration will show that an interpolated value between appreciable corrections is just as reliable as an interpolated value between small corrections.

VIII. Testing Equipment

The baths used for testing are of two general types; one type for reproducing fixed points, the other for comparison of thermometers with previously standardized thermometers.

A. Ice Bath. A convenient method for reproducing the ice point and for measuring the changes in bulb volume already referred to is the use of the ice bath. A Thermos bottle or Dewar flask, mounted in an upright position, serves as a container for the ice, the melting of the ice being retarded by the insulating properties of such vessels. The ice, shaved from clear cakes, and distilled water are mixed to form a slush. Enough water is used to afford good contact with the thermometer bulbs, but not so much as to float the ice. From time to time excess water is drained off by means of a glass syphon to which is attached a length of rubber tubing closed with a pinchcock. Precautions are taken to prevent contamination of the ice and water. A small reading telescope with a magnification of about 10 diameters makes for more accurate reading both because of the magnification so obtained and the aid afforded in the elimination of errors in reading due to parallax. Gently tapping the thermometer just before the reading may prevent sticking of a falling meniscus.

B. Steam Bath. The steam point may be realized in a steam-point apparatus or hypsometer either by comparing the thermometers with standards or by the determination of the temperature of steam at the prevailing pressure.

The bath consists of a double-walled steam jacket in which steam from a boiler circulates. The thermometers are suspended in such a manner as to insure free circulation of the steam around them. Provision is made either for relieving or determining any excess pressure in the space surrounding the thermometers.

When a steam bath is used as a fixed-point apparatus, a barometer is a necessary piece of equipment, since the true temperature of the steam must be determined by ascertaining the prevailing pressure from the barometric readings. The usual corrections are applied to the barometer reading, including any corrections necessary for the local value of gravity, for difference in height of the steam bath and the barometer and for any excess pressure in the hypsometer. The steam temperature is then found from pressure-temperature values in Table 7, reproduced from a paper by Osborne and Meyers.[15] This procedure is capable of an accuracy of 0.002 to 0.003 °C on the International Temperature Scale. The Fortin type barometer is generally available and serves for all but the most exacting measurements.

The steam bath may also be used as a comparator, in which case the temperature of the steam is determined at the time of test by means of a previously standardized thermometer.

C. Comparators. Stirred liquid baths of two designs are used at the National Bureau of Standards as comparators in which thermometers in the range from −40 to 500 °C are compared. This equipment is of appropriate design to accommodate the thermometers to be tested, to permit adequate stirring for uniform temperature distribution and to provide for heat input regulation for temperature control.

A type suitable for use for media which do not solidify at room temperatures, shown in Fig. 1 [16] is constructed from two tubes of different diameters with connecting passages at the top and bottom. The heating coil, cooling coil for circulating ice water for comparisons below room temperatures, and stirrer are located in the smaller tube, the larger tube being left clear for immersion of the thermometers.

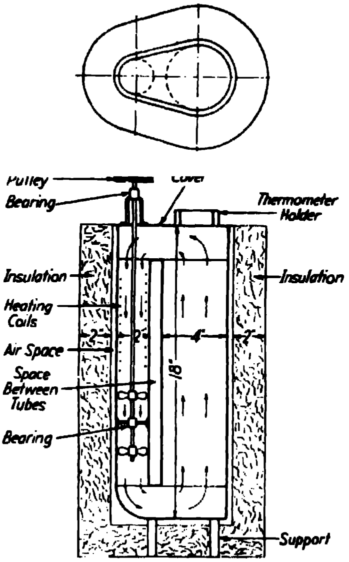

Fig. 1. Stirred liquid bath. Two tubes connected at top and bottom.

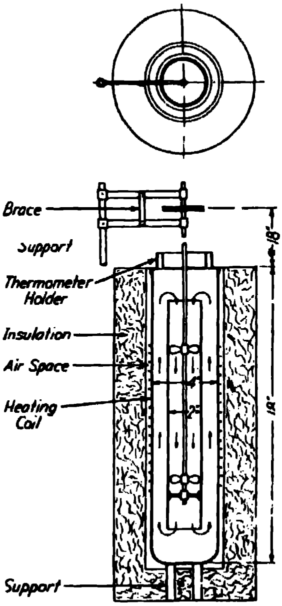

Fig. 2. Stirred liquid bath. Two coaxial tubes.

The type shown in Fig. 2,[16] built from two coaxial tubes with passages at the top and bottom, permits use of media which solidify upon cooling to room temperatures. The propeller is mounted very near the bottom of the inside tube leaving the space above it free to receive thermometers.

The diameters of the large and small tubes of the container shown in Fig. 1 are 8¾" and 4" respectively, and the container is 24" deep. Fig. 1 shows a design suitable for use with either water or oil. The outside tube of the design illustrated in Fig. 2 is 5½" in diameter and the inside one 3¾"; the container is 20" deep.

The stirrers, of the propeller type, are located centrally in the smaller tubes. For adequate stirring, these tubes should have a cross-sectional area not less than ⅛ of the cross-sectional area of the bath and it need not be greater than ¼ of the cross-sectional area of the bath. The upper and lower ends of a stirrer tube should terminate a distance about equal to or somewhat less than its own diameter from the top and bottom of the bath. For such arrangements a propeller speed of about 400 to 600 rpm should provide adequate stirring. In the type of bath shown in Fig. 1, with downward flow in the stirrer tube, the propeller also serves to mix the liquid which has first passed over the temperature control coils.

For comparisons in the range 5 to 95 °C or 40 to 200 °F water is used as the medium in which to realize the temperatures. For temperatures from about 105 to 315 °C or 220 to 600 °F an oil having the following properties is used:

Flash point (Pensky-Martens closed cup)	185 °C (365 °F)
Flash point (Cleveland open cup)	196 °C (385 °F)
Fire point (Cleveland open cup)	218 °C (425 °F)
Viscosity [Saybolt Universal at 99 °C (210 °F)]	43 sec.

This oil is somewhat too viscous to stir well at 100 °C, gives off considerable vapor at temperatures above 200 °C and requires precautions against ignition, either communicated or spontaneous. As a precaution against ignition the oil should be well covered, if heated above its flash point, both during use and after partial cooling. After use the container should be covered with as nearly as possible an air-tight lid, since the vapors filling the space above the contracting liquid ignite readily in the presence of even small quantities of air. At the higher temperatures the oil gradually loses the properties essential to thermometer testing purposes and requires replacement.

Above 315 °C, in the type of bath shown in Fig. 2, the medium used is molten tin which is allowed to solidify when not in use. The heating coil, wound around the outside of the tank, melts the tin nearest the outside wall first, and no expansion difficulties are encountered. When molten, the tin, surrounding the tubes or wells in which the thermometers are mounted, serves as a means of obtaining a uniform temperature in which comparisons with standard thermometers are made for any test point up to 500 °C or 930 °F. Since the thermometers are not immersed directly in the tin but in tubes closed at the bottom, they are compared, in reality, in an air bath. It should be emphasized that in this method the tin is never used for fixed-point determinations.

Molten salts may be used in high-temperature baths. Sodium or potassium nitrate or a mixture of these have been used and may be preferred. Neither tin nor the salt mixture is entirely satisfactory and the choice between them is largely a matter of individual preference.

Electrical heating is used in all the baths described. For the water and oil baths a bare ribbon wound on insulating material is mounted in the stirrer tube ahead of the propeller. The tin container is wrapped on the outside with a tape of Nichrome, or other resistance alloy of similar type, mica-insulated, and held in place with Alundum paste. The resistor, used on alternating current, in the water bath is made of an alloy ribbon of 60% gold, 40% palladium. An alloy of 90% platinum, 10% rhodium would also serve. The resistors used in the oil bath are wound of Nichrome ribbon. For rapid heating between test points, a line voltage of 220 volts is used directly across the coils; for maintaining very slowly rising temperatures at the test points, a transformer with a variable secondary voltage provides regulation from zero up to the voltage needed at the highest temperature at which tests are made.

A two- or three-inch thickness of insulation, held in place by a double-walled compartment so that it will not have to be disturbed when repairs on the tank proper are necessary, reduces heat loss and aids in maintaining uniform temperature distribution. Ground cork serves for insulating material below 100 °C and such materials as asbestos, magnesia mixtures, diatomaceous earth, rock wool or slag wool, expanded vermiculite and others serve for the higher temperatures at which cork would char. The tops of the baths are provided with covers, insulated, and arranged to carry holders which may be rotated by means of bevel gears to bring successive thermometers into view of a vertically adjustable telescope.

Tests at temperatures above 500 °C or 930 °F are made in a copper cylinder, wound with an electrical resistance ribbon, more closely spaced at the ends than in the middle to compensate for cooling at the ends. The whole is covered with a two-inch thickness of insulation. Holes parallel to the axis and of sufficient size to receive the thermometers serve for immersion wells. Since the temperature may not be uniform over the length of the cylinder, care must be taken that all bulbs are immersed to the same depth, and unless the thermometers are identical in design, stem temperatures must be considered.

Tests at temperatures below 0 °C to about −40 ° are made in a stirred liquid bath of the same general type as the one shown in Fig. 1. The bath is cooled by regulation of the flow of carbon dioxide under pressure through an expansion valve, and temperature regulation both at test points and for a more rapid change between points can be obtained by supplementary electrical heating. A 75% carbon tetrachloride, 25% chloroform mixture provides a non-flammable liquid for temperatures as low as −59 °C (−74 °F), and has a viscosity sufficiently low at all temperatures down to its freezing point to permit effective stirring. A list of liquids suitable for such uses has been given in a paper by Kanolt.[17]

Apparatus suitable for comparing thermometers with similar standards has been described in a paper by Mueller and Wilhelm.[16]

Equipment adapted for testing at temperatures below −40 °C is described in a paper by R. B. Scott of the National Bureau of Standards.[18]

IX. Standards

The standardization of a thermometer consists of comparing its indications directly or indirectly with those of a standard platinum resistance thermometer at a sufficient number of points so that interpolated values between test points may be considered reliable.

The working standards of the National Bureau of Standards comprise, in addition to the standard platinum resistance thermometers, a number of mercury-in-glass thermometers chosen so that the range covered by each of a series of thermometers is subdivided into intervals appropriate for its range. The resistance thermometers are calibrated at the fixed points designated on the International Temperature Scale and therefore define that scale. The mercury-in-glass standards, compared with the resistance thermometers, also reproduce the International Scale to the accuracy which may be expected from the various types and ranges. Ice-point determinations after use and periodic complete re-calibration of the resistance thermometers serve to give assurance that the coefficients have remained constant or to indicate a change, should any occur. Ice- or other reference-point readings on mercury-in-glass standards are made after each or each alternate test point so that changes in bulb volume may be known and allowed for in addition to the calibration corrections.

A. Total Immersion Standards. The National Bureau of Standards maintains a series of total immersion thermometers, graduated in suitable divisions for the intervals covered, which serve as standards for total immersion comparisons. The series covers the ranges listed and is subdivided as shown below.

−40	to	22 °C	in	0.2 °
−1		51		0.1
49		101		0.1 with auxiliary scale at 0 °C
−2		102		0.2
98		202		0.2 with auxiliary scale at 0 °C
195		320		0.5 with auxiliary scale at 0 °C
295		510		1.0 with auxiliary scale at 0 °C

B. Partial Immersion Standards. Like standards, maintained for the testing of accepted designs of partial immersion thermometers, are standardized for stem-temperature conditions prevailing during use. This procedure permits the direct comparison of results of similar thermometers, as long as the bulbs are at the same temperature and the stem temperatures are essentially the same for all the thermometers under comparison. An additional advantage is that like standards eliminate many of the precautions necessary when checking dissimilar thermometers.

X. Special Thermometers

A. Beckmann Thermometers. A metastatic or Beckmann thermometer is usually of the enclosed-scale type, so constructed that a portion of the mercury may be removed from the bulb in order that the short scale may be used for differential measurements at various temperatures over a limited range. The large bulb is joined to the fine capillary, backed by the milk glass scale, by a capillary of much larger diameter. The glass used in the construction of these instruments is Jena 16^{III} or its American equivalent, Corning normal. A scale length of 5 or 6 °C serves the purpose of the Beckmann thermometer. The "setting" of the thermometer refers to the temperature of the bulb when the reading is 0° on the scale.

If a Beckmann thermometer is used at partial immersion, the large capillary joining the bulb and the small capillary is the source of some uncertainty, since the temperature of this relatively large quantity of mercury, enclosed in the glass case, cannot be actually measured. Reduction of the size of this capillary would increase the accuracy of the instrument.

Calibration of a Beckmann thermometer by comparison at every degree on the scale with a standardized platinum resistance thermometer is of an accuracy sufficient for most purposes. A slightly more accurate, but also more hazardous, calibration may be made by first determining irregularities in the capillary by means of short mercury threads whose length is observed at various positions on the scale, and combining the data so obtained with the correction for the mercury-in-glass to the accepted temperature scale and the corrections for error in length of one scale degree as compared with a standard thermometer.

When the setting of a Beckmann thermometer is changed to allow for use at a higher or lower temperature, the quantity of mercury affected by any temperature change is different. It follows that two equal changes in temperature at different settings cause a different indication on the scale. Therefore a "setting factor" must always be used to convert reading differences into true temperature differences whenever the thermometer is used at any setting different from the one for which it was designed to read true temperature differences, or at a setting different from the one at which it was calibrated. These setting factors combine corrections for the different changes in volume of different quantities of mercury during equal temperature changes, and the difference between the mercury-in-glass and the accepted scale.

Although the computation of the table of setting factors now in use was based on the old international hydrogen scale, which is now replaced by the International Temperature Scale, defined by means of a standardized platinum resistance thermometer, they are still applicable. The intercomparisons of the mercury-in-Jena 16^{III} glass and the standard scale have been most accurately and painstakingly carried out in the range 0 to 100 °C. Since most differential measurements, as in calorimetry, which are made with Beckmann thermometers, are carried out in this range, it has seemed unnecessary to extend the range of the setting factors beyond that of the usual one, 0 to 100 °C. An explanatory sheet listing these setting factors and supplied with each Beckmann tested by the National Bureau of Standards is reproduced here. The "corrections from the preceding page" and "Correction from certificate" mentioned on this sheet refer to the calibration corrections obtained during test and shown on the document issued with each Beckmann thermometer tested.

A second sheet explaining the correction for emergent stem for calorimetric, differential or Beckmann thermometers, and issued in addition to the setting factor sheet, is also reproduced here.

"This sheet gives a table of setting factors and an example to explain the processes employed in calculations. The example, however, has not been specifically adapted to the individual thermometer with which this sheet is issued.

"The thermometer is said to have a given setting, for instance 20 °C, if its scale reading is 0° when the temperature of the bulb is 20 °C.

"The following table, calculated for thermometers of Jena 16^{III} glass, gives a series of factors corresponding to different settings by which each observed temperature difference must be multiplied after applying the corrections given on the preceding page. This factor is made unity for a setting of 20 °C.

For any scale length up to 15'

Setting (°C)	Factor	Setting (°C)	Factor
0	0.9931	55	1.0094
5	0.9950	60	1.0105
10	0.9968	65	1.0115
15	0.9985	70	1.0125
20	1.0000	75	1.0134
25	1.0015	80	1.0143
30	1.0029	85	1.0152
35	1.0043	90	1.0161
40	1.0056	95	1.0169
45	1.0069	100	1.0177
50	1.0082		

"As an illustration, suppose the following observations were made:

Setting.......... = 25 °C. Lower reading = 2.058°
Stem temperature = 24° Upper reading = 5.127°

	Lower	Upper
Observed reading =	2.058	5.127
Correction from certificate =	+.005	−.008

Corrected upper reading = 5.119
Corrected lower reading = 2.063

Difference = 3.056
Setting factor 1.0015 corr. = +.005
Emergent stem correction* = +.004

Corrected difference = 3.065

* See accompanying stem correction sheet.

"The corrections for inequalities of the bore were determined by calibration with two mercury threads 0.5° and 2.5° in length. The value of the mean scale degree at setting 25 °C was determined by comparison with a standard platinum resistance thermometer.

"At setting 25.00 °C, 5.037 mean scale degrees were found equal to 5.046 °C."

"Differential Correction for Emergent Stem

"This sheet is designed to explain a convenient process of computing the differential correction for emergent stem but has not been specifically adapted to the individual thermometer with which it is issued.

"If a calorimetric or differential or a metastatic (Beckmann) thermometer is actually used with a part of its stem emergent from the bath, a differential stem correction must be calculated and applied as explained below, making use of the formulas there given.

"Example 1.—Suppose the point, I°, to which the thermometer was immersed was 16 °C; its initial reading, T°_1, was 24.127°; its final reading, T°_2, was 27.876°; the mean temperature, t°, of the emergent stem was 26°; then—

"Differential stem correction $= 0.00016\ (28 - 24)\ (24^\circ + 28^\circ - 16^\circ - 26^\circ) = +\ 0.006^\circ$.

"The result, 0.006°, should be added to the difference between T°_2 and T°_1, found after applying to each the corrections tabulated under "Results of Test" on the certificate or report.

"Example 2.—Suppose a Beckmann thermometer was immersed to the 0° mark on its scale; its initial reading T°_1, was 2.058°; its final reading T°_2 was 5.127°; the mean temperature, t°, of the emergent stem was 24 °C; and the setting, S°, was 25 °C; then—

"Differential stem correction $= 0.00016\ (5–2)\ (25^\circ + 2^\circ + 5^\circ - 24^\circ) = +0.004^\circ$.

"The result $+0.004^\circ$, should be added to the difference between T°_2 and T°_1, found after applying to each the corrections tabulated under "Results of Test" in the certificate or report, and multiplying the difference by the setting factor (1.0015 for a setting of 25°)."

"Explanatory Notes on the Emergent Stem Correction

"Calorimetric and differential and metastatic (Beckmann) thermometers are pointed and graduated by the makers to read correct or approximately correct temperature intervals when the bulb and the entire mercury index in the stem are exposed to the temperature to be measured, and such thermometers are standardized for the condition of "total immersion," and the corrections given in certificates or reports apply for the condition of total immersion.

"In practically all cases, however, such thermometers are actually used with only the bulb and a portion of the stem immersed, the remainder of the stem projecting into the air above the bath.

"In such cases the accuracy attained can be increased by applying the necessary corrections for the emergent stem. The emergent stem correction corresponding to any reading may be computed by means of the formula—

$$\text{Stem correction} = K \times n(T^\circ - t^\circ)\ ;$$

where K = the differential expansion coefficient of mercury in glass;
= 0.00016 for centigrade thermometers;
= 0.00009 for Fahrenheit thermometers;
n = number of degrees emergent from the bath;
T° = temperature of the bath;
t° = mean temperature of the emergent stem.

"However, in differential measurements the parts of the scale on which readings are made are, in general, emergent from the bath and it is usually permissible to assume that t° will be constant during the measurement. In this case, instead of calculating the stem corrections for the initial and final readings, and applying them separately, the differential stem correction can be more conveniently computed by using the appropriate formula of the two given below.

"**Differential emergent stem correction for ordinary thermometers.**—The differential stem correction may be computed from the following formula:

$$\text{Differential stem correction} = K \times d(T^\circ_1 + T^\circ_2 - I^\circ - t^\circ);$$

K = 0.00016 for centigrade thermometers;
= 0.00009 for Fahrenheit thermometers;
T°_1 = the initial reading;
T°_2 = the final reading;
$d = T^\circ_2 - T^\circ_1$;
I° = scale reading to which the thermometer was immersed;
t° = mean temperature of the emergent stem.

"It should be noted that this differential stem correction, as well as the difference d°, may be either positive or negative, and the correction must be applied with due regard to these signs.

"**Differential emergent stem correction for metastatic (Beckmann) thermometers.** The differential emergent stem correction may be computed from the following formula, provided the thermometer is immersed to its 0° mark:

$$\text{Differential stem correction} = K \times d(S^\circ + T^\circ_1 + T^\circ_2 - t^\circ);$$

where S° = the "setting" of the thermometer, and K, d, T°_1, T°_2, and t° have the meanings given in the preceding paragraph.

"It should be noted that this differential stem correction, as well as the difference d, may be either positive or negative, and the correction must be applied with due regard to these signs.

"A Beckmann thermometer of the ordinary type should not be used with any part of the lower portion of the stem exposed, as this part may contain from 5 to 10 times as much mercury per centimeter as the graduated portion, and if exposed introduces a large and uncertain error.

"In case it is necessary to use such a thermometer with some of the lower portion of the stem emergent from the bath, the necessary correction may be computed from the above formula, provided S° in the formula is replaced by $S^\circ + m^\circ$, where m is the number of degrees the temperature of the thermometer must be *lowered* to bring the meniscus from the zero position on its scale to the point of immersion.

"If the thermometer is immersed to some point other than its 0° mark, as would ordinarily be the case with thermometers having the 0° graduation at the top of the scale, the differential stem correction may also be computed from the above formula, provided S° in the formula is replaced by $S^\circ + m^\circ$, where m is the number of degrees the temperature of the thermometer must be *lowered* to bring the meniscus from the zero position on its scale to the point of immersion. Provided the points at which readings are made are above the point to which the thermometer is immersed, the preceding statement is applicable whether the point to which the thermometer is immersed is on the scale or below it."

B. Calorimetric Thermometers. Three types of calorimetric thermometers designed for use for measurements of temperature differences are available.

For use with the Gas Calorimeter:
ranges 45 to 100 °F in 0.1°
60 to 110 °F in 0.1°

Note: A specification for thermometers differing somewhat from the above is in process of preparation.

Centigrade Calorimetric Thermometer:
range 18 to 31 or 32 °C in 0.02°
Fahrenheit Calorimetric Thermometer:
range 65 to 90 or 105 °F in 0.05°

Table 6, reproduced from B. S. Circular No. 8,[13] gives the tolerances for this type of thermometer. "In calorimetric or differential thermometers the accuracy at any one temperature is of less importance than the accuracy of the temperature intervals. This table gives the tolerances for the temperature intervals of some typical differential thermometers."[18]

Table 6. Tolerances for Calorimetric and Differential Thermometers.[18]

No. of degrees on scale	Graduation interval in degrees	Allowable change in correction in degrees	Accuracy of interval in degrees	Corrections stated to
20-45 °F	0.05	0.08 over a 5° interval	0.01-0.02	0.01
10-20 °C	.02	0.03 over a 2° interval	.005-.01	.002
5-6 °C (Beckmann type)	.01	0.01 over a 0.5° interval for setting of 20°	.002-.005	.001

No tolerances for scale error are given in the table, although it is desirable that the scale error be small.

C. Industrial Thermometers. Industrial or metal-protected mercury- (or other liquid-) in-glass thermometers are adapted for use in plant or shop work where ruggedness is necessary but where high precision is not of paramount importance. Thermometers of this type cover a working range from about −40 to 500 °C and are graduated for partial immersion of the liquid column.

The essential departures of this type of thermometer from the usual liquid-in-glass type are the protection features, namely, the heavy metal back scale, with large and distinct graduations and figures, the metal protection tube for the stem and bulb, and the threaded connections for convenience in installing the instrument in the apparatus where it is to be used. Such thermometers may be fitted directly into the apparatus or into separable sockets which permit their removal without interfering with the functioning of the apparatus.

The protecting enclosure around the bulb retards heat transfer between the bulb and the medium, the temperature of which is to be measured. This retardation has two effects: first, the bulb may not, even after a very long time, assume the temperature of the medium, if there is any appreciable heat flow along the thermometer; second, the time lag of the thermometer is greater than it would be if the bulb were immersed directly. Both of these undesirable effects can be made smaller by filling the space between the bulb and its protecting enclosure with a good conductor of heat, or by making the protecting enclosure to fit the bulb with very little clearance.

Other factors which may influence the readings are variations in the construction of the protecting case; the material in which the bulb enclosure is immersed, such as liquid, vapor or gas; the rate of flow of the material past the bulb; and the conditions surrounding the emergent stem.

Because the factors mentioned above may affect the indications of industrial thermometers appreciably, such thermometers cannot be depended upon for reliable temperature values unless they have been calibrated and standardized under conditions the same as those of use. If the thermometers are used to indicate temperature changes only, it may not be necessary to consider all the sources of error mentioned.

D. Clinical Thermometers. Clinicals, or medical thermometers, are small maximum reading thermometers used in measuring body temperatures. The range of scale covers some 10 degrees Fahrenheit, from at least 96 to 106 °F, or 6 degrees centigrade from at least 35 to 41 °C.

The bulb, made of a suitable grade of thermometric glass, has the least volume, that is, the least heat capacity consistent with a reasonably steady motion of the mercury along the very fine capillary of the lens front tubing. A constriction above the bulb fashioned by collapsing a bubble blown in the capillary permits the expanding mercury to pass when the bulb is being warmed, but is "tight" enough to prevent it from retreating after the warming ceases. The constriction must be "loose" enough so that the mercury can be shaken back by applying mechanical force, either by shaking down by hand or by whirling in a suitable centrifuge.

The function of the clinical thermometer, *i.e.*, to indicate the temperature of the body, requires that the thermometer be left in place for a time sufficiently long so that all the mercury has reached the body temperature. This requires, for most thermometers, three minutes or more.

Testing by the National Bureau of Standards is not required by law, although such instruments as are submitted for that purpose will be accepted for test for a nominal fee. Thermometers meeting the requirements are certified and a mark ("NBS40," this year), is placed on the thermometer to show this fact. A note explaining the certification is issued with each thermometer certified.

State regulations controlling the sale of clinicals within their boundaries, are in effect in Connecticut, Michigan, and Massachusetts. Such regulations permit, through properly authorized laboratories, the licensing of manufacturers. Only the product of manufacturers licensed by the state may be sold legally within the boundaries of that state.

A National Bureau of Standards publication, Commercial Standard CS1-32,19 gives detailed test requirements of this Bureau.

XI. Separated Columns

Many inquiries are received concerning separated mercury columns, particularly after shipment. Since no means of avoiding such occurrences has yet been found, the recourse of stating some directions for joining the mercury is adopted. The mercury may separate somewhat more readily in thermometers which are not pressure-filled, but it can be more easily joined since there is little gas to separate the liquid. The process of joining broken columns consists of one or a series of manipulations which may be effective, and these are briefly described here.

1. The bulb of the thermometer may be cooled in a solution of common salt, ice and water (or other cooling agent) to bring the mercury down into the bulb. Moderate tapping of the bulb on a paper pad or equally firm object or the application of centrifugal force usually serves to unite the mercury in the bulb. If the salt solution does not provide sufficient cooling, carbon dioxide snow (dry ice) may be used. Since the temperature of dry ice is about −78 °C and mercury freezes at about −40 °C, it will cause the mercury to solidify. Care must be taken to warm the top of the bulb first so that pressures in the bulb due to the expanding mercury may be relieved. Care should also be taken in handling dry ice as it may cause severe "burns."

2. If there is a contraction chamber above the bulb or an expansion chamber at the top of the thermometer the mercury can sometimes be united by warming the bulb until the column reaches the separated portions in either enlargement. Great care is necessary to avoid filling the expansion chamber completely with mercury, which might produce pressures large enough to burst the bulb. Joining the mercury is more readily accomplished if the quantity in either cavity has first been shattered into droplets by tapping the thermometer laterally against the hand.

3. As a last resort, especially for thermometers having no expansion chambers, small separated portions of the column can sometimes be dispersed by warming, into droplets tiny enough to leave space for the gas to by-pass, and these droplets can then be collected by a rising mercury column.

The procedure for thermometers in which organic liquids are used is similar. Liquids in the stem can more readily be vaporized and may then be drained down the bore. The latter process is aided by cooling the bulb. All of these manipulations require patience, and experience is helpful, but they will yield results if care is used. A convenient method of ascertaining that all the liquid has been joined is a check of the ice point, or some other point on the scale.

XII. Specifications

Recently there has been an increased tendency toward the design of a suitable thermometer for the specific work involved. This tendency should not be overdone, and much time and some expense can doubtless be saved by scrutiny of the several lists of thermometer specifications already available. Types of thermometers available may be found in current issues of catalogs published by firms handling such items, and detailed specifications in the publications of societies such as the American Society for Testing Materials. However, if no available thermometer is suitable and a new specification must be resorted to, it is best to develop a specification which will enable and require the manufacturer to furnish thermometers which will satisfy the important requirements.

The sample form shown below covers the required information and complies essentially with the form used by the manufacturers. Delays can therefore be avoided if the specifications are written in this form originally.

The sample specification shown here is intended to serve merely as a pattern, to illustrate the form found useful. It will be noted that the length of a degree on the scale is fixed by the dimensional specifications included.

Specification for Laboratory Thermometer

Type: Etched stem, glass.
Liquid: Mercury.
Range and subdivision: 195 to 320 °C in 0.5° with auxiliary scale from −2 to +5 °C.
Total length: 395 to 400 mm.
Top finish: Glass ring.
Immersion: Total.
Stem: Plain front, enamel back, suitable thermometer tubing, diameter 6 to 7 mm.
Bulb: Corning normal or equally suitable thermometric glass, length 15 to 20 mm, diameter 5 to 6 mm.
Distance from bottom of bulb to beginning of unchanged capillary above the enlargement, not greater than 80 mm.
Length of unchanged capillary above or below the zero degree line, not less than 15 mm.
Distance to 195 degree line from unchanged capillary above the enlargement, not less than 60 and not greater than 80 mm.
Length of unchanged capillary between the highest graduation line and the expansion chamber, not less than 10 mm.
Distance to 320 degree line from top of the thermometer, not less than 40 nor more than 80 mm.
Filling above mercury: Nitrogen or other suitable inert gas.
Graduation: All lines, figures and letters to be clear cut and distinct. The graduation lines to be fine, straight, of uniform width and perpendicular to the axis of the thermometer. The first and each succeeding 5° line to be longer than the rest and to be numbered. Each degree line to be shorter than the 5° lines but longer than the half degree lines. The bulb shall be thoroughly annealed before the thermometer is graduated to minimize subsequent changes in indications.

Special marking: A serial number and the manufacturer's name or trade mark shall be etched on the stem.

Scale error: The scale error at any point shall not exceed 1.0 °C.

These thermometers shall be high grade laboratory instruments.

Note: For the purpose of interpreting these specifications the following definitions apply.

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

XIII. Tables

Table 7. (Thermometric) Condensation Temperature of Steam. [15]

[Star (*) indicates change in integer]

P	Pressure in mm mercury (standard)										P
	0	1	2	3	4	5	6	7	8	9	
	Temperature in degrees of International Scale										
500	88.678	.730	.782	.834	.886	.938	.990	*.042	*.093	*.144	500
510	89.196	.247	.298	.350	.401	.452	.502	.553	.604	.655	510
520	.705	.756	.806	.856	.907	.957	*.007	*.057	*.107	*.157	520
530	90.206	.256	.306	.355	.405	.454	.503	.553	.602	.651	530
540	.700	.749	.798	.846	.895	.944	.992	*.041	*.089	*.138	540
550	91.186	.234	.282	.330	.378	.426	.474	.521	.569	.617	550
560	.664	.712	.759	.806	.854	.901	.948	.995	*.042	*.089	560
570	92.136	.182	.229	.276	.322	.369	.415	.462	.508	.554	570
580	.600	.646	.692	.738	.784	.830	.876	.922	.967	*.013	580
590	93.058	.104	.149	.195	.240	.285	.330	.375	.420	.465	590
600	.5100	.5548	.5996	.6443	.6889	.7335	.7780	.8224	.8668	.9112	600
610	.9554	.9996	*.0438	*.0879	*.1319	*.1759	*.2198	*.2636	*.3074	*.3511	610
620	94.3948	.4384	.4820	.5255	.5689	.6123	.6556	.6989	.7421	.7852	620
630	.8283	.8713	.9143	.9572	*.0001	*.0429	*.0857	*.1284	*.1710	*.2136	630
640	95.2562	.2987	.3411	.3834	.4257	.4680	.5102	.5523	.5944	.6365	640
650	95.6785	.7204	.7623	.8041	.8459	.8876	.9293	.9709	*.0125	*.0539	650
660	96.0954	.1368	.1782	.2195	.2607	.3019	.3431	.3842	.4252	.4662	660
670	.5072	.5480	.5889	.6297	.6704	.7111	.7517	.7923	.8329	.8734	670
680	.9138	.9542	.9946	*.0349	*.0751	*.1153	*.1555	*.1956	*.2356	*.2756	680
690	97.3156	.3555	.3954	.4352	.4749	.5146	.5543	.5939	.6335	.6730	690
700	.7125	.7519	.7913	.8307	.8700	.9092	.9484	.9876	*.0267	*.0657	700
710	98.1048	.1437	.1827	.2216	.2604	.2992	.3379	.3766	.4153	.4539	710
720	4925	.5310	.5695	.6079	.6463	.6846	.7229	.7612	.7994	.8376	720
730	.8757	.9138	.9519	.9899	*.0278	*.0657	*.1036	*.1414	*.1792	*.2170	730
740	99.2547	.2924	.3300	.3675	.4051	.4426	.4800	.5174	.5548	.5921	740
750	.6294	.6667	.7039	.7410	.7781	.8152	.8523	.8893	.9262	.9631	750
760	100.0000	.0368	.0736	.1104	.1471	.1838	.2204	.2570	.2936	.3301	760
770	.3666	.4030	.4394	.4758	.5121	.5484	.5846	.6208	.6570	.6932	770
780	.7293	.7653	.8013	.8373	.8733	.9092	.9450	.9808	*.0166	*.0524	780
790	101.0881	.1238	.1594	.1950	.2306	.2661	.3016	.3371	.3725	.4079	790
	0	1	2	3	4	5	6	7	8	9	

Washington, March 30, 1934.

Table 8. Emergent Stem Correction Factors for Centigrade Thermometers.[7]

Mercury-in-glass Thermometers

$\frac{T+t}{2}$ °C	Verre dur	Jena 16^{III}	Jena 59^{III}	Jena 1565^{III}	Jena Combustion
50	0.000158	0.000158	0.000164	0.000172	0.000164
100	158	158	164	172	164
150	158	158	165	173	165
200	159	159	167	175	167
250		161	170	177	171
300		164	174	180	174
350			177	184	178
400			182	188	182
450			187	194	188
500			195	200	195

Other Liquid-in-glass Thermometers

$\frac{T+t}{2}$ °C	Pentane	Toluene	Alcohol
− 180	0.0009		
− 160	09		
− 140	09		
− 120	10		
− 100	10		
− 80	10	0.0009	0.0010
− 60	11	09	10
− 40	12	10	10
− 20	13	10	10
0	14	10	10
+ 20	15	11	10

The data for Jena 16^{III} glass and Jena 59^{III} may be used for Corning normal and Corning borosilicate thermometer glasses respectively.

For computations in Fahrenheit temperatures, the proper value of the factor is 5/9 of the tabulated value.

Table 9. Values of $t - t_{g1}$ for Mercury-in-Glass Thermometers.[7]

t = temperature on accepted scale, t_{g1} = temperature on mercury-in-glass scale.

t°	French hard (verre dur)	Kew glass	Jena 16^{III}	59^{III}	Jena 1565^{III}	Jena combustion
− 39	+0.420					
− 30	+ .290		+0.28	+ 0.13		
− 20	+ .172		+ .16	.07		
− 10	+ .073		+ .07	+ .03		
0	.000	.00	.00	.00	0.00	0.00
+ 10	− .052	.00	− .06	− .02	− .03	
20	− .085	.00	− .09	− .04	− .05	
30	− .102	+ .005	− .11	− .04	− .06	
40	− .107	+ .01	− .12	− .03	− .06	
50	− .103	+ .01	− .12	− .03	− .05	
60	− .090	+ .01	− .10	− .02	− .04	
70	− .072	+ .015	− .08	− .01	− .03	
80	− .050	+ .02	− .06	.00	− .02	
90	− .026	+ .025	− .03	+ .02	− .01	
100	.000	.00	.00	.00	.00	0.00
120	+ .06		+ .03	− .05	+ .06	
140	+ .07		+ .02	− .16	+ .03	
160	+ .03		− .02	− .31	− .13	
180	− .04		− .12	− .52	− .38	

Table 9.—(*Continued*)

t °C	French hard (verre dur)	Kew glass	Jena 16^{III}	Jena 59^{III}	Jena 1565^{III}	Jena combustion
200	− .12		− .29	− .84	− .90	− 1.13
220			− .5	− 1.3	− 1.3	− 1.6
240			− .9	− 1.9	− 1.8	− 2.2
260			−1.4	− 2.6	− 2.4	− 3.0
280			−2.0	− 3.4	− 3.1	− 4.0
300			−2.7	− 4.4	− 3.9	− 5.1
320				− 5.8	− 4.8	− 6.4
340				− 7.2	− 5.9	− 7.8
360				− 8.8	− 7.3	− 9.5
380				−10.6	− 8.9	−11.4
400				−12.6	−10.5	−13.5
420				−14.9	−12.4	−15.9
440				−17.4	−14.7	−18.6
460				−20.2	−17.2	−21.5
480				−23.3	−20.0	−24.8
500				−26.9	−23.1	−28.4
550					−32.	−39.
600					−44.	
650					−58.	

Table 10. Values of $t - t_{gl}$ for Other Liquid-in-Glass Thermometers.

t	Pentane in 16^{III} glass	Toluene in verre dur	Alcohol in verre dur
−190	−23.4		
−180	−21.0		
−170	−18.6		
−160	−16.2		
−150	−13.9		
−140	−11.6		
−130	− 9.4		
−120	− 7.3		
−110	− 5.3		
−100	− 3.4		
− 90	− 1.7		
− 80	− 0.2	0.0	
− 78.5	0.0	0.0	0.0
− 70	1.0	.4	+0.3
− 60	2.0	.8	+ .6
− 50	2.6	1.1	+ .7
− 40	3.0	1.2	+ .9
− 30	2.9	1.2	+ .9
− 20	2.4	1.0	+ .8
− 10	1.5	0.6	+ .5
0	0.0	0.0	.0
+ 10	2.0		
20	4.4		
30	7.6		−3.6
100		−24.4	

"In Tables 9 and 10, t represents the temperature on the standard working scale (platinum resistance thermometer) except for verre dur, where t represents temperatures on the former International hydrogen scale, which in practice is not distinguishable from the standard reference scale, while t_{gl} represents corresponding temperatures on the several liquid-in-glass scales."[7]

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Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance

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Introduction

The progressive depression of the temperature which occurs during the freezing of a substance has long been recognized as affording a measure of the amount of impurities which the substance contains. White[1] has given a rather detailed discussion of the theoretical aspects of this use of the freezing behavior of substances. His discussion is illustrated with obervations on substances sufficiently impure to make very precise thermometric measurements unnecessary. The present paper describes an apparatus and technic designed for the determination of concentrations of impurity of 0.01 mole per cent or less.

The general equation for lowering of the freezing point of a pure substance by a solute which forms an ideal or sufficiently dilute solution in the liquid phase of the substance, but does not form a solid solution with it, is[2]

$$R \ln(1 - x) = \Delta C_p \ln \frac{(T_{f_0} - \Delta t)}{T_{f_0}} - \frac{L_{f_0} - \Delta C_p(\Delta t)}{T_{f_0} - \Delta t} + \frac{L_{f_0}}{T} \tag{1}$$

in which x is the mole fraction of the solute; T_{f_0} is the freezing point of the pure substance on the Kelvin scale; $\Delta t = T_{f_0} - T_f$, where T_f is the initial freezing temperature (the temperature at which an infinitely small quantity of solid is in equilibrium with the solution); L_{f_0} is the molal heat of fusion of the pure substance; ΔC_p is the molal heat capacity of the liquid substance minus that of the solid; and R is the gas constant. If this equation is put in the form of a series we have

$$x(1 + \tfrac{1}{2}x + \tfrac{1}{3}x^2 + \qquad \frac{L_{f_0}\Delta t}{RT^2_{f_0}}\left[1 + \left(\frac{1}{T_{f_0}} - \frac{\Delta C_p}{2L_{f_0}}\right)\Delta t + \left(\frac{1}{T^2_{f_0}} - \frac{2\Delta C_p}{3L_{f_0}T_{f_0}}\right)(\Delta t)^2 + \cdots\right] \tag{2}$$

By neglecting terms with powers higher than the second, an equation can be written in the form*

$$x = \frac{L_{f_0}}{RT^2_{f_0}}[\Delta t - a(\Delta t)^2], \tag{3}$$

in which the value of a is given by

$$\frac{}{2RT^2_{f_0}} - \frac{1}{T_{f_0}} + \frac{\Delta C_p}{2L_{f_0}}.$$

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* Acknowledgment is made to W. G. Schlecht for reducing equation (1) to this form. The equation corresponding to (3), which expresses Δt in terms of x, is

$$\Delta t = \frac{RT^2_{f_0}}{L_{f_0}}(x + bx^2), \text{ in which the value of } b \text{ is given}$$

by

$$\tfrac{1}{2} - \frac{RT}{2L^2_{f_0}}(2L_{f_0} - T_{f_0}\Delta C_p), \text{ which usually differs very little from } \tfrac{1}{2}.$$

The part $\left(-\frac{1}{T_{f_0}}+\frac{\Delta C_p}{2L_{f_0}}\right)$ can usually be neglected, leaving

$$a=\frac{L_{f_0}}{2RT^2_{f_0}}.$$

In almost all cases when the foregoing equations might be used to calculate the purity of a substance, x is so small that second power terms of Δt can also be neglected, in which case we have the equation which is commonly used,

$$x=\frac{\Delta t L_{f_0}}{RT^2_{f_0}}. \tag{4}$$

To determine the content of impurities in a substance from its initial freezing temperature, it would be necessary either to measure this temperature accurately and to have an equally accurate independent value of T_{f_0}, or to compare (with out regard to the accuracy of the two values) the initial freezing temperature with that of a sample of the substance of known purity. Adequately accurate values of T_{f_0} are seldom available and, likewise, samples of known purity are not often at hand. In any case, it is practically impossible to observe the initial freezing point because of the difficulty of getting equilibrium when only a negligible amount of the solid phase has appeared. Ordinarily, the initial freezing temperature is obtained by extrapolation from the observations made as freezing progresses but, to do this accurately, one must take into account such matters as the degree of undercooling and the fact that, even after freezing begins, the observed temperatures will depart slightly from the true temperature of equilibrium.

Instead of determining the initial depression, use may be made of the difference between the extrapolated initial freezing temperature and the temperature at a stage of freezing when the mass of remaining liquid is in some simple ratio to the entire mass of the substance. Assuming that, as freezing progresses, only pure solvent separates, and therefore that the concentration of impurities increases inversely as the proportion of substance remaining unfrozen, the depression of the freezing point when half of the substance is frozen will be twice the initial depression.* Therefore, the difference between the initial freezing temperature and the temperature at the half-way point will be equal to the initial depression. Similarly, the change from the initial freezing temperature to the temperature when three-fourths of the substance is frozen is three times the initial depression.

Obviously it is possible to use the decrease in temperature between any two stages of freezing, if the respective proportions frozen are known, thereby eliminating extrapolation to the initial freezing temperature. An equation for this purpose is

$$x=\frac{(T'-T'')}{(y''-y')}\frac{L_{f_0}}{RT^2_{f_0}} \tag{5}$$

in which T' and T'' are the freezing temperatures at two successive stages of freezing, and y' and y'' are the ratios of the total mass of substance to the mass of liquid remaining unfrozen at those stages.

General Discussion of the Method and of Sources of Error

To use the freezing range to determine relatively small concentrations of impurities demands enough of apparatus and technic that the method is not likely to be used for substances to which more common methods of examination, such as chemical analysis, are applicable. Further, the method has certain limitations which restrict its field of usefulness. One obvious limitation is that the substance must not undergo a significant degree of decomposition or other alteration of its molecular structure during the freezing period (or the period during which it is prepared for freezing), and that the concentration of impurities must not change because of vaporization. Another is that the method does not apply to types of impurities which form solid solutions with the substance or to systems which depart significantly from the behavior of an ideal, or sufficiently dilute, solution. However, there are many substances, particularly organic compounds, whose purity cannot be readily measured by other methods, at least with the same degree of accuracy. The formation of solid solutions appears to be uncommon among systems of organic compounds. Even when solid solutions are found, as White * has pointed out, the freezing curve will often serve to disclose impurities, although not to determine their concentration (unless the identity of the impurity is known). Perfectly flat freezing curves can occur only with pure substances and certain extremely unusual systems, such as solid solutions of substances of identical freezing points, or systems having compositions which correspond exactly to a maximum or a minimum point in a freezing temperature-composition diagram.

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* W. P. White[1] apparently was the first to make use of this simple relation.

In the measurement and interpretation of freezing ranges by the methods already mentioned there are a number of sources of error, of which the important ones, other than the fundamental limitations already discussed, are as follows:

1. *Uncertainty as to the proportion frozen at any given time.* It is not permissible to assume that the substance freezes at a constant rate, and thus that the proportion of substance remaining unfrozen [or y in Equation (5)] can be calculated directly from the time elapsed since the beginning of freezing.† Even if a constant difference were maintained between the temperature of the freezing substance and that of the cooling bath, the rate of freezing would change progressively as freezing proceeds. The accumulation of solid on the walls of the vessel retards the loss of heat, and the change in volume on freezing (almost always negative) changes the level of the liquid and hence the effective area in contact with the cooling bath. The usual effect of estimating the proportion frozen from elapsed time, either on the assumption that the initial rate of loss of heat is maintained or by White's method,[1] is to make the concentration of impurity appear too large. Such errors may be small at the incorrectly estimated mid-point of freezing, but become progressively greater at later stages.

2. *Difference between measured temperatures and equilibrium temperatures.* Since heat is constantly being withdrawn from it, the temperature of the system must be lower by a small but unknown amount than the true temperature of equilibrium between the liquid and solid phases. This difference may not be the same at different stages of freezing. To keep it as constant (and preferably as small)

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* See reference 1.

† The time required for freezing is sometimes calculated by multiplying the time in which the liquid cools 1°, in the vicinity of the freezing point, by the ratio between the heat of fusion and the specific heat of the liquid. A large error may be introduced by ignoring the specific heat of the cell. The rate of loss of heat can be determined much more exactly by immersing a small heating coil in the liquid, and measuring the electrical energy necessary to keep the same thermal head that is to be maintained during freezing.

W. P. White[1] observes the complete freezing curve and part of the cooling curve of the solid, and from these observations calculates the time required to freeze any given proportion of the substance. He assumes that the rate of loss of heat is constant throughout the entire freezing process, except for the change in rate which results from a change in thermal head, and the secondary effect of the difference between the specific heats of the liquid and solid.

as possible, thorough stirring of the liquid, or mixture of liquid and crystals, is essential.* Some types of substances, such as certain hydrocarbons, are so viscous at the freezing temperature that adequate stirring may be impossible. Further, the rate of crystallization of these substances may be too slow to maintain thermal equilibrium at any practicable rate of loss of heat.

3. *Departure from the condition that only pure solvent separates.* At any finite rate of freezing there must be some departure from the idealized condition that the crystals, as they form, do not carry with them any of the impurity (by adsorption, for example) or trap any of the liquid. This departure may not be proportional to the concentration of the impurity.

4. *Progressive departure from the behavior of an ideal solution.* During freezing, the solution may depart progressively from the idealized behavior represented by Equation (1). This departure depends on the nature of the constituents of the solution, as well as on the concentration.

5. *Inadequate precision in the thermometric measurements.* The necessary precision of measurement to get a desired precision in the determination of x can be derived from Equation (5). This will determine the choice of measuring instrument. Since only differences in temperature are measured, the instrument need be calibrated only on a relative basis.

6. *Lack of adequate knowledge of the properties of the substance.* In some instances the heat of fusion of the substance may not be known with adequate accuracy to get a desired accuracy in the determination of x [Equation (2)]. Uncertainties in the values of T_{f_0} and of ΔC_p are of vanishingly small importance.

Of the errors arising from the sources enumerated, No. 1, which relates to the uncertainty concerning the proportion of liquid frozen at any given time, may be large, especially if more than half of the freezing range is used. The error from this source, together with errors arising from No. 2 and No. 6, and in part from No. 3, can be largely eliminated by a procedure in which the freezing range of the substance is compared with that of an identical sample to which has been added a known concentration, a, of some substance† selected to behave, as closely as possible, in accordance with Equation (1). If the conditions of freezing are well enough reproduced, the increase in the change of freezing temperature between any two timed stages of freezing will be proportional to the concentration of the added substance. If T'_x and T''_x represent two freezing temperatures of the original substance, and $T'_{(x+a)}$ and $T''_{(x+a)}$ represent the freezing temperatures observed after the addition of the known concentration of "impurity," at exactly corresponding stages of freezing, then

$$\frac{x}{a} = \frac{(T' - T'')_x}{(T' - T'')_{x+a} - (T' - T'')_x}. \tag{6}$$

This procedure reduces the errors from several sources, but it is subject to the one listed as No. 4. However, this error can be minimized by care in selecting the impurity to be added and by using no greater concentration of it than is needed to get the desired precision in the term $(T'-T'')_{x+a} - (T' - T'')_x$.

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* In preliminary work, attempts to measure the freezing range of benzoic acid without stirring were wholly unsuccessful. The thermometer was provided with a silver collar, with radial fins extending into the freezing substance, to promote thermal equilibrium. The conductivity of non-metallic substances generally is too small to maintain thermal equilibrium without stirring during any reasonable period of freezing, except possibly when the distances are very small.

† If the identity of the impurity is known, it is obviously desirable to add more of the same impurity.

Apparatus and Technic

The measurements which will be used to illustrate the freezing procedure were made with a 25-ohm platinum resistance thermometer of the coiled filament type described by Meyers,[3] in conjunction with a thermostated Mueller bridge and a galvanometer which gave a scale deflection of 1 to 2 mm at a distance of 1 m for a change in resistance of 0.0001 ohm (0.001 °C). In later work the length of the optical lever was increased to about 5 m and a reversing switch was used, so that the total deflection was about 35 mm for a change in resistance of 0.0001 ohm. The thermometer and bridge were suitably calibrated to yield values for small differences in temperature to a precision of about 0.0001 °. The material used was benzoic acid identified as National Bureau of Standards Standard Sample No. 39e, which is issued as a standard substance for calorimetry and acidimetry. Phthalic anhydride and anthracene were the substances added in known concentrations to cause the increase in the temperature difference $(T'-T'')$.

The resistance coil of the Meyer's thermometer occupies a space about 2 cm long in a glass tube 7 mm in diameter. The thermometer was centered in a cylindrical glass freezing tube 2 cm in diameter * and about 25 cm long, provided with a glass jacket which could be evacuated, if desired, to decrease the rate at which heat is lost. The thermometer was supported by a ground-in glass head which was provided with inlet and outlet tubes for the passage of dried air through the upper part of the freezing cell. The tip of the thermometer was about 2 cm from the bottom of the cell. At the beginning of freezing the depth of liquid in the cell was about 11 cm (this required 35 grams of benzoic acid). Just above the bottom of the freezing cell was situated a glass gas-bubbler of the type recently described by Branham and Sperling,[4] with orifices about 0.003 inch in diameter. The bubbler was provided with an inlet tube passing through the double-walled vessel and connected to a source of purified air which was finally dried by passing it through a glass-wool filter cooled by liquid air. The stream of air served both to remove water † from the liquid benzoic acid before freezing and to stir the substance during freezing. Stirring with a stream of air, introduced at the same temperature as that of the cooling bath, was found to cause more rapid agitation of the freezing liquid than a reciprocating spiral stirrer which was used at first, and permitted freezing of a larger proportion of the sample. If a large enough sample was used so that the final liquid level provided sufficient immersion for the thermometer, more than 90 per cent of the sample could be frozen. The mechanical stirrer usually stopped operating not long after the mid-point of freezing was reached. Furthermore, the upward motion of the stem of the stirrer carried some liquid above the surface at each stroke and thereby probably caused non-equilibrium freezing of an unknown amount of the sample. Because the orifices of the bubbler were so small, only about two liters of air per hour was required for rapid stirring. The stream of air (introduced at the temperature of the cooling bath) therefore did

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* This diameter provides enough space for a mechanical stirrer. When the liquid is stirred with a stream of gas bubbles, the apparatus can be made smaller, so as to require less material, but then it will not be possible to freeze as large a proportion of the sample.

† Almost all organic liquids absorb some water, and liquid benzoic acid is notably hygroscopic. The depression of the freezing point of benzoic acid in equilibrium with air saturated with water at 0° and at 20° indicated a solubility of water in benzoic acid (at about 130°), under partial pressures of 4.6 and of about 18 mm of water vapor, of 0.050 and 0.20 mole per cent, respectively. Extrapolation to one atmosphere of water vapor yields a value of 8 mole per cent (1.2 per cent by weight).

not dissipate a significant part of the total heat given off, either because of its own heat capacity or by vaporization of benzoic acid.

In preparation for freezing, the benzoic acid was kept about 10° above its freezing point (122.4 °C) in an air bath while the stream of thoroughly dried air * was passed through it to remove water taken up by the acid during preliminary melting in contact with moist air. The rate at which this water was removed depended, of course, on the volume of dry air used and the size of the bubbles. No exact observations were made, but the passage of air in fine bubbles for 2½ to 3 hours, at a rate of about 2 liters per hour, removed nearly all the water. Longer passage of air caused only slight changes in the apparent purity of the acid as judged from differences in the freezing curves of different samples.

When the substance was ready for freezing, the apparatus was transferred to a well-stirred oil bath, which was kept, within a few thousandths of a degree, at a temperature selected to give the desired initial rate of freezing. For the work reported in this paper, the thermal head between the freezing cell and the bath was about 4 °C. Since the temperature of the bath was kept constant, the thermal head decreased slightly as freezing progressed. For the same reason the thermal head was also slightly less when a sample containing more impurity was frozen. The time required for complete freezing was about 3 hours.† Since there were only small openings in the glass head, and a positive pressure of air was always maintained within the apparatus, there was no opportunity for the diffusion of oil vapors or other impurities into it.

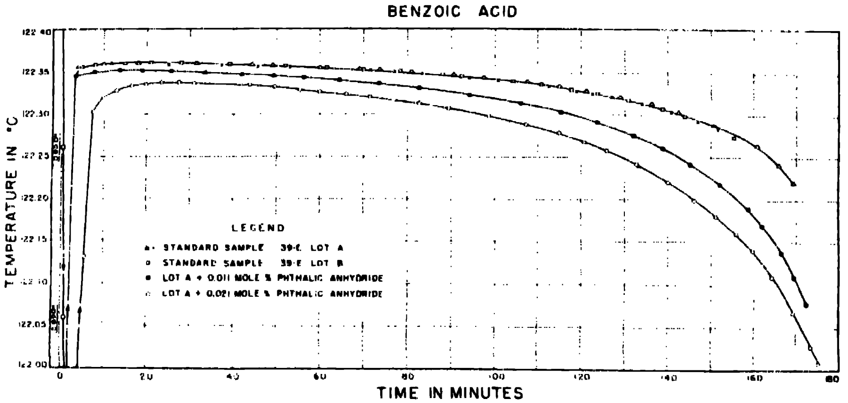

FIG. 1. Curves showing freezing temperatures of benzoic acid plotted with respect to elapsed time.

The kind of cooling curves obtained is illustrated by Fig. 1. The acid always undercooled about 0.5°, after which the temperature usually rose very sharply to within a few thousandths of a degree of the highest point on the freezing curve. To get a sharp and reproducible recovery from undercooling, it was found necessary to have the outside wall of the cell at very nearly uniform temperature before the

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* The method of purifying the air, as well as certain other details of procedure, will be described in a later paper contemplated for publication in the *Journal of Research of the National Bureau of Standards.*

† The time calculated on the assumption that heat was lost at a constant rate, measured at the beginning of freezing, was about 2 hours.

cell was placed in the cooling bath. A further refinement of technic was to induce, by seeding, the beginning of freezing at a given stage of undercooling.

As freezing progressed, the resistance of the thermometer was measured at frequent intervals. At first the time corresponding to a selected change in resistance was recorded, and all the curves in Fig. 1 represent observations made in this way. In later practice, the resistance was measured at selected times, so as to get values for temperature which could be used directly, instead of interpolated values, in calculating the concentration of impurities.

Illustrative Data on Benzoic Acid

The uppermost curve in Fig. 1 represents three sets of observations. Two of these (represented by the symbols x and Δ) were made on successive days with the same sample (lot A). Separate curves for these two sets of data would be identical, within the precision of measurement, at their highest points and 0.002° apart after freezing had progressed for 150 minutes. This difference may indicate a slight increase in the purity of the benzoic acid (of the order of 0.0004 mole per cent) between the two freezings. On the other hand the difference between the two curves may only reflect variations in the conditions of freezing. The observations represented by the symbol □ were made on another portion of the same benzoic acid (lot B), after two preliminary freezings, the results of which were rejected because recovery from undercooling was not rapid enough to indicate satisfactory conditions of freezing. A curve drawn through the points marked □ would be identical within 0.001° with a curve through the points marked X, throughout the entire range.

The three sets of observations indicate that the benzoic acid did not undergo significant changes in composition during the treatment to which it was subjected between successive freezings. This is believed to justify the assumption that it also underwent no significant change during the subsequent treatment involved in two successive freezings, after the addition of phthalic anhydride and anthracene.

Table 1. Estimation of the Concentration of Impurities in Benzoic Acid by Comparison of Freezing Ranges (Additions of Phthalic Anhydride).

Time interval (min.)→	30–50	50–70	70–90	90–110	110–130	130–150	30–150
$(T' - T'')_x$ degrees	0.0031	0.0042	0.0064	0.0106	0.0170	0.0314	0.0727
$(T' - T'')_{x+a}$ degrees	.0052	.0075	.0114	.0179	.0293	.0533	.1246
$(T' - T'')_{x+b}$ degrees	.0048	.0103	.0157	.0222	.0357	.0638	.1525
Mole fraction of impurity*	.00016	.00014	.00014	$.00016_0$	$.00015_2$	$.00015_7$	.000154
Mole fraction of impurity†	.00038	.00014	.00014	.00019	.00019	.00020	.00019

$$^{*}\ a\,\frac{(T' - T'')_x}{(T' - T'')_{x+a} - (T' - T'')_x}$$

$$^{\dagger}\ b\,\frac{(T' - T'')_x}{(T' - T'')_{x+b} - (T' - T'')_x}$$

$a = 0.00011_0$ mole fraction of phthalic anhydride.
$b = 0.00021_2$ mole fraction of phthalic anhydride.

The curves in Fig. 1 which are identified by the symbols ● and ○, respectively, represent the results obtained on twice re-freezing lot A after adding, successively, 0.011_0 and 0.010_2 mole per cent of phthalic anhydride. It will be noted that the recovery from undercooling after the first addition of phthalic anhydride was identical within the limits of observation with that which occurred before, but that a slower recovery occurred after the second addition. The maximum of the curve representing the second addition was reached much later than with the other curves. This curve is included to illustrate the importance of establishing reproducible conditions in the early stages of freezing. The curve, and the numerical results which it represents (see Table 1), show that it cannot validly be compared with the others.

In Table 1 are given the numerical values for changes of temperature which occurred during the second freezing of benzoic acid, lot A, and the freezings after the two additions of phthalic anhydride, together with estimates of the concentration of impurities in the original material which are based on these values. Temperatures measured during the first 30 minutes of freezing were not used in the calculations because recovery from undercooling was going on during much of this interval. In the later stages of freezing the observed temperatures were undoubtedly subject to a small but progressive error because of the decreasing immersion of the thermometer. It is believed that in the observations made up to 150 minutes the errors from this source were less than other small errors, such as those arising from differences in the rates of freezing (caused by small differences in the thermal head). Each numerical value was obtained by linear interpolation between the two temperatures observed nearest to the selected time. Since the observed temperatures were at random intervals, interpolation may have caused small variable errors. There may also be an uncertainty of 0.00002 or 0.00003 ohm in the measurements of relative resistance, corresponding to 0.0002 and 0.0003° in the observed temperatures.

Table 2. Estimation of the Concentration of Impurities in Benzoic Acid by Comparison of Freezing Ranges (Additions of Anthracene).

Time interval (min.)→	30–50	50–70	70–90	90–110	110–130	130–150	30–150
$(T' - T'')_x$ degrees	0.0030	0.0045	0.0070	0.0109	0.0179	0.0319	0.0752
$(T' - T'')_{x+a}$ degrees	.0058	.0083	.0131	.0193	.0314	.0562	.1341
$(T' - T'')_{x+b}$ degrees	.0079	.0119	.0168	.0268	.0459	.0803	.1896
Mole fraction of impurity*	.00014	.00015	.00015	$.00016_6$	$.00017_0$	$.00016_8$	.000163
Mole fraction of impurity†	.00016	.00016	.00019	$.00018_7$	$.00017_2$	$.00017_7$	.000177

* $a \dfrac{(T' - T'')_x}{(T' - T'')_{x+a} - (T' - T'')_x}$

$\overline{(T' - T'')_{x+b} - (T' - T'')_x}$

$a = 0.00012_8$ mole per cent of anthracene.
$b = 0.00026_9$ mole per cent of anthracene.

Table 2 contains the results obtained when successive additions of 0.012_8 and 0.014_1 mole per cent of anthracene were made to benzoic acid, lot B, except that observations of freezing temperatures for the additions were made at exact 10-minute intervals (as well as others) and hence are not subject to the errors of interpolation.

Calculations of the concentration of impurities are based on six 20-minute intervals, as well as on the entire 2-hour interval. Consideration of the short intervals helps to disclose irregularities, and also trends, in freezing behavior. The irregular variations in the estimates of purity based on the ratio x/b for the various intervals in Table 1 confirm the faults of the curve for the second addition of phthalic anhydride, which have already been discussed. The estimates based on the ratio x/a, in Table 1, show no irregularity within their relative precision.

There is evidence of a slight positive trend, as freezing progresses, in the estimates shown in Table 2. In the later stages of freezing, after the two additions of anthracene, there was enough decrease in the thermal head to retard somewhat the progress of freezing. Consequently, the proportion of solid was not quite the same at any given point on these freezing curves as at the corresponding time on the curve for the original material. Therefore, changes in temperature for equal intervals of time on the curves are not strictly comparable. If the results were corrected for the effect of the decreased thermal head, each successive temperature difference would be slightly greater, as would also the difference for the entire period of 30-150 minutes. Correspondingly, the estimates of the concentration of impurity in the original material which are based on the later intervals, and on the whole 2-hour period, would be decreased somewhat. It is obviously difficult to make a rigorous correction for this effect, but an approximate calculation indicates that the interval 30-150.8 minutes should be used for the first addition of anthracene, and 30-151.6 minutes for the second addition, instead of 30-150 minutes. The correspondingly corrected estimates of the concentration of impurity in the original material are 0.000156 and 0.000164 mole fraction, respectively, instead of 0.000163 and 0.000177.

Apart from the experimentally difficult procedure of maintaining a strictly constant thermal head as freezing progresses, the error in question can be largely eliminated by using a larger thermal head, or by comparing only the earlier portions of the freezing curves. If the thermal head is larger a given change in the head necessarily will have a smaller effect on the rate of freezing. If desired, the original rate of loss of heat can be maintained by simultaneously decreasing the thermal conductivity of the jacket of the cell (by a suitable degree of evacuation).

There is an unexplained irregularity in the middle portion of the freezing range observed after the second addition of anthracene. The estimates based on this set of observations should be given less weight than those based on the first addition of anthracene and the first addition of phthalic anhydride.

The most concentrated solution whose freezing temperature was used in these calculations occurred when freezing had progressed for 150 minutes, after the second addition of anthracene. At this point the mole fraction of combined solutes in the remaining liquid was about 0.0025. The maximum effect of neglecting the second power term* of Equation (3) in estimating the concentration of impurities in the benzoic acid from the data in Table 2 is less than two parts in one thousand.

The results reported in this paper have pointed the way to further refinements of technic which may increase the reliability of this procedure for estimating the purity of substances. If so, these refinements will be reported in a later paper, in which attention will also be given to a comparison of the procedure with the estimation of purity based on the change in the apparent specific heat of a solid substance at temperatures approaching its melting point.

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* The numerical form of Equation (3) for benzoic acid is $x = 0.013_3\,\Delta t - 0.00008_0(\Delta t)^2$, taking $L_{f_0} = 17{,}300 \pm 500$ joules, $\Delta C_P = 87 \pm 2$ joules, and $T_{f_0} = 395.5°$.

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Potentiometers for Thermoelectric Measurements

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Potentiometers specially adapted for thermoelectric work have been known for 30 years; the present discussion, therefore, will partly summarize and I hope clarify somewhat things familiar to many of you.

Thermel, a word in use now for 20 years, will be used as a shorter equivalent or abbreviation of the term of more evident meaning, *thermoelectric thermometer.* This older expression is so long that it seemed handicapped in competition with shorter ones, such as *thermocouple.* The shorter words, however, each described some one form of thermoelectric thermometer; there was formerly no short term meaning a thermoelectric thermometer in general, and the attempt to use the special terms for that purpose created much confusion. It is possible to restrict *thermocouple* to its original and logical meaning, a thermel of two wires only; when it is desired to speak of thermoelectric thermometers in general, without distracting the attention over temporarily irrelevant details, *thermel,* or *thermoelectric thermometer,* can be used.

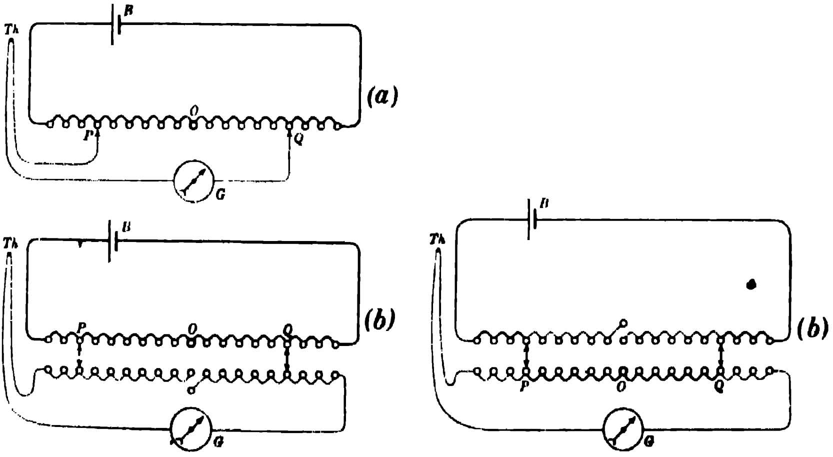

Fig. 1. (a) Elementary potentiometer; (b, left) same, plus Brooks' arrangement for nearly constant galvanometer circuit resistance; (b, right) same, with Diesselhorst's terminal decades putting the switches in the battery circuit.

The Problem

The measurement of the electromotive force of a thermel is, after all, just another electromotive force measurement. It usually can be done, after a fashion, by almost any potentiometer. The problem it presents is the small magnitude of the force. This calls for one feature of the simplest character and no difficulty: the extension of the range to low values. It calls also for another, more exacting one: the exclusion of unwelcome, intruding, or "vagabond" electromotive forces, more menacing on account of the smallness of the forces being measured. The special features of design which characterize potentiometers for thermel work are, with one or two exceptions, entirely determined by the need to diminish or exclude these intruders. The intrusive electromotive forces are of two kinds: one, voltage drop through the variable resistances of switches; two, thermoelectromotive forces, especially in the contacts at switches. Thus in Fig. 1a, which you will recognize as nearly the most elementary potentiometer possible, perhaps the majority of instruments in use being represented by it, the switches *P* and *Q*, with their contact surfaces, lie in the galvanometer circuit, in series with the thermel; hence this form of instrument is not satisfactory for precise work. On the other hand, these switches carry practically no current; consequently their resistance causes no potential drop.

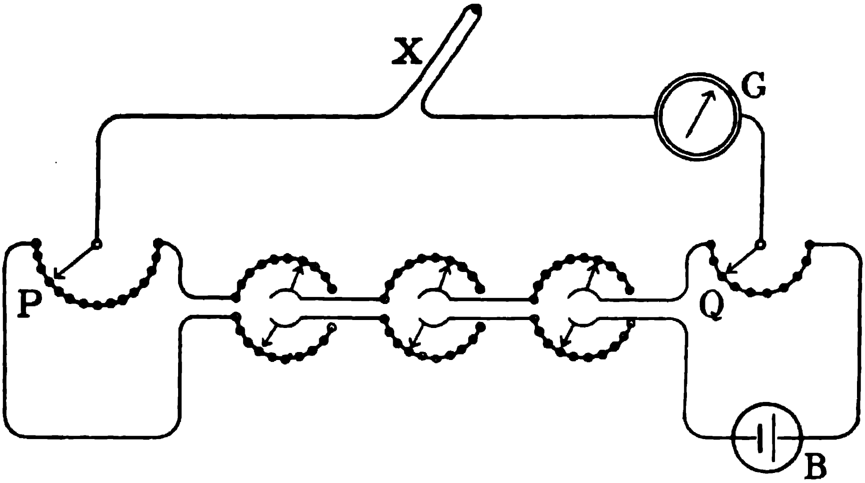

FIG. 2. General plan of Feussner-Wolff potentiometer.

The resistance difficulty entered as soon as the effort was made to get a greater range—that is, to add other dials. Many of you must have personal recollection of that majestic battleship among potentiometers, the Fuessner-Wolff of 30 or more years ago. In that, as you of course know if you ever looked inside the thing, the two decades of our Figure 1a were separated, and three decades inserted between them. Here the resistance of the three switches—six contacts in all—and worse than that, their variations, were always in that part of the standard current circuit which was also in the galvanometer circuit. The detrimentally high resistance used —10,000 ohms per volt—was designed to make the switch resistance insignificant by comparison, but even that did not succeed very well. Many of you may remember the morning ritual of cleaning and oiling switches which was needed to get proper results with the Wolff. This may be compared with the White potentiometer, which gave me perfect performance literally for ten years without even a look at the dial switches.

This comparison illustrates an interesting fact: the success of potentiometers specially designed for thermoelectric and other low-voltage work was due not to unprecedented refinement in the construction of switches and other parts, but to devices or arrangements which put the switches where they could not do harm.

The 1905 to 1907 Development

The beginning came in 1905, in an article by H. Hausrath,[1] which proposed the three most important of the eight devices which can be recognized as fundamental. Things then began moving fast. The next year, 1906, Diesselhorst, at the Reichsanstalt, described a 5-dial potentiometer [2] in which two of Hausrath's devices were used to get three decades totally free from intrusive electromotive forces in the switches. He had nothing as good for the other two decades. The next year I showed how this deficiency could be remedied, approximately,[3] by applying to potentiometers a device already used in other apparatus, pointing out also that all the new devices gave nearly constant galvanometer circuit resistance, and therefore permitted constant sensitiveness, with the galvanometer becoming more valuable than two decades of coils. Within six months Diesselhorst [4] had made, tested, and described in print a 5-dial instrument embodying these suggestions. This was so good a job of designing that the instrument, I am told, has been made from that day to this with hardly any change.

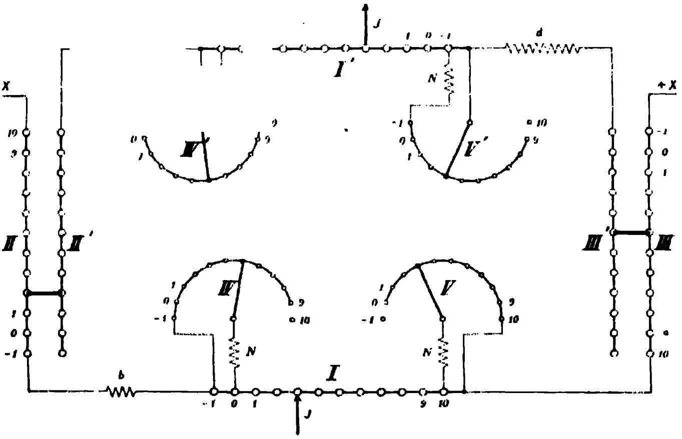

FIG. 3. Diesselhorst's 1908 potentiometer, with his terminal decades, Hausrath's split-circuit decade, and two pairs of Waidner-Wolff decades.

Meanwhile, in the Geophysical Laboratory of the Carnegie Institution of Washington, there was in use a potentiometer utilizing the third of Hausrath's fundamental suggestions, the instrument named by Mr. Morris E. Leeds the "White Potentiometer." This had a further new feature in being a double potentiometer. Thus in two and a half years there had been perfected the prevailing low-voltage potentiometers, as they were to be for the next 20 years. A year or so later, also in the Geophysical Laboratory, two "Wenner" potentiometers were constructed, having a new feature of great ingenuity and appreciable usefulness.[5]

Of the six special devices used in low-voltage potentiometers, the one universally employed is putting the switches of the terminal decades in the galvanometer circuit. Fig 1b, right, shows one way, Diesselhorst's, of doing it. It is interesting to compare this with Fig. 1b, left, (H. B. Brooks), which is Fig. 1a, with the galvanometer circuit made nearly constant.

A second Hausrath device is dividing the circuit through part of the potentiometer, as shown in Fig. 3, which is Diesselhorst's final design. The current flows through the switches *JJ*, which move together in opposite directions. Since

JJ remain at the same potential, shifting them changes the potential of $-X$ and $+X$ in the galvanometer circuit. The resistance and possible electromotive force of the switches are quite outside the galvanometer circuit.

The split circuit has another value, which Hausrath may not have seen. Resistances can now be put in the galvanometer (and battery) circuit which still leave the zeros of decades II and III at the same potential, but which, when their values are changed by shunting, change the potential of II and III. Such resistances are shown in decades IV and V. They are the Waidner-Wolff elements whose insertion I suggested in 1907. The resistance and thermal force of the switches are not fully removed from the galvanometer circuit, but their effects are attenuated by their being in series with the high-resistance shunts. The galvanometer-circuit resistance is changed, but only slightly, by the adjustment of these lower decades.

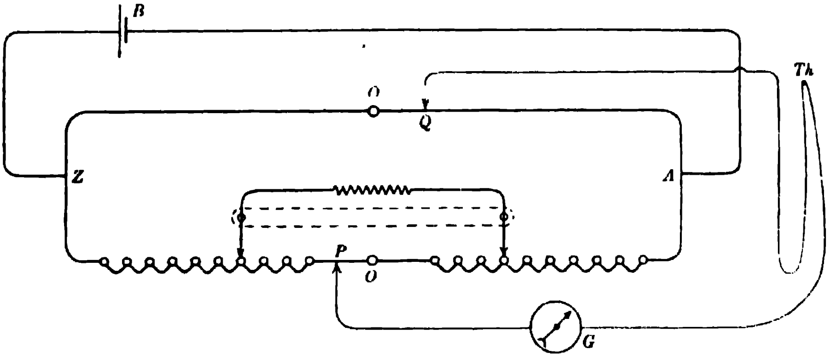

FIG. 4. Split circuit and one Wenner decade.

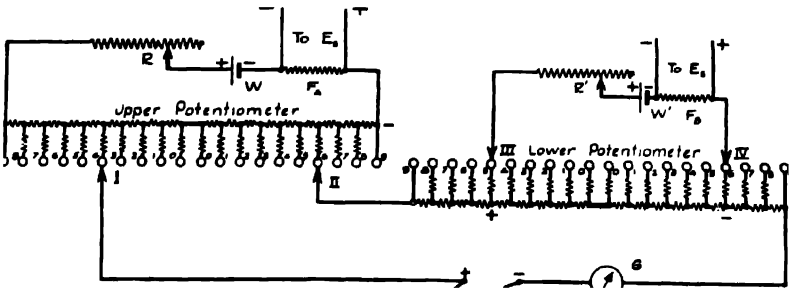

FIG. 5. Principle of the White potentiometer.

The Wenner element, Fig. 4, is a superior but not indispensable substitute for the Wolff-Waidner. The figure, for simplicity, shows one in use, where two are usually employed, and more may be. The split circuit is again split, with two currents flowing past *O*, one through *O*, the other through the shunt. Where both currents flow through any one of the small coils, the potential drop through it is greater, and the number of coils thus affected depends on the position of the shunt.

Hausrath's third device, the foundation of the White potentiometer, Fig. 5, is merely putting two of the simplest kind of potentiometer, each with its battery, into the same galvanometer circuit.[6] As carried out here, the lower potentiometer has the switches in the battery circuit as usual, but the upper potentiometer puts them in the galvanometer circuit (1) better to insure constant battery current, and (2) to permit a truer realization of constant galvanometer sensitiveness. The "compensation tract" (where the galvanometer and battery circuits coincide) is shunted by the path through the battery, so that the galvanometer circuit resistance is not quite constant for unvarying coils in the galvanometer circuit. Of course this arrangement is not vital. The coils shown here as vertical are a scheme original with this potentiometer. They perform the same function as different coils in Fig. 1. Their advantage is in simplifying the switches, which is important in simplifying the master switch for the double potentiometer. Such simple switches, also, can be relatively inexpensive, and can require extraordinarily little attention. I have had a set of them work perfectly for literally 10 years with not even any inspection.

Later Additions

The devices just described have held the field for nearly 30 years. Two others may now come into general use. One is an end-decade, invented, but not used, by Diesselhorst in 1906, and re-invented by I. M. Stein, who has patented a potentiometer using it in a form slightly modified to facilitate construction. This decade is just one coil in the galvanometer circuit, lying also in a closed ring containing 9 or 10 equal coils (Fig. 6). As current is led in at different points around the ring, the current, and therefore the voltage drop, in the single coil change by equal steps. The advantage is that the entire galvanometer circuit tract consists of only four coils, which are easily shielded thermally by a metal box, so as to minimize intrusive thermal forces. Such shielding is an important part of a development which is now beginning to bring potentiometer performance beyond the point reached in 1910.

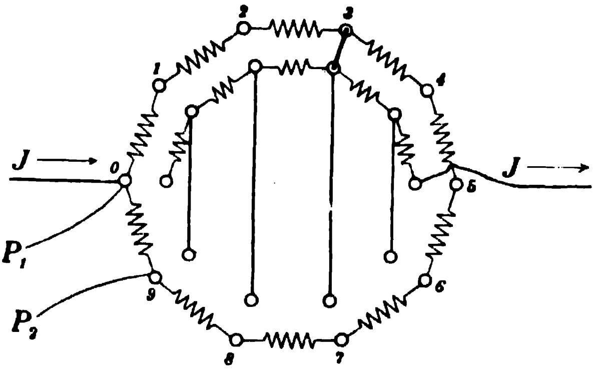

FIG. 6. Diesselhorst-Stein ring element. Coil O-9 only in galvanometer circuit. Current through it is changed to change the emf reading.

The other device, commonly called a "Lindeck," is Poggendorff's "Second Method" of 1841, developed into a simple potentiometer by Lindeck in 1900, now applied as one dial in a modern potentiometer[7] (Fig. 7). The potential drop through a single coil is adjusted by varying a current which is read by an ammeter.

Annexed to another potentiometer, this arrangement surpasses the galvanometer in replacing two lower decades, the galvanometer then becoming merely a null instrument. Its great advantage, apparently, is in avoiding all careful adjustment of the galvanometer circuit resistance, so that it is a welcome alternative for anyone whenever he has to work with numerous different pieces of apparatus. On the other hand, I think we can see how it may impede rapid work, especially when different thermels are read alternately and repeatedly. Without it, we throw a switch, the galvanometer deflects; as soon as it comes to rest, we read, almost instantaneously. With the Lindeck, we must adjust till the galvanometer is at zero, which involves waiting for the period of the galvanometer, probably more; then when the adjustment is made the Lindeck is still to be read. It may to some sound ridiculous to mention the time required to move the observer's head from the galvanometer telescope to the proper place over the ammeter, but we are now dealing with a matter of seconds, anyway. The decisive consideration seems to be that for the rapid and repeated readings it will usually be easy to adjust the galvanometer circuit resistance closely, so there would be little need of the Lindeck, whatever the amount of delay it causes. Its aid in the cases where it is valuable can be gratefully welcomed.

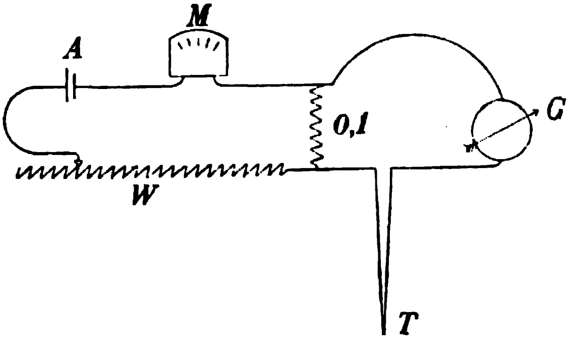

FIG. 7. Lindeck potentiometer. Voltage drop in coal 0,1 is measured as ammeter *M* measures the current through it.

Further Progress

The precision obtained by some recent potentiometers is probably a greater ratio of increase over the 1907 types than they were over their predecessors, although positive statements are here hard to be sure about. The improvement, since intrusives in the switches had already been eliminated, was obtained through dealing with the coils by the very unspectacular means of thermal shielding, and by winding the coils so that the two ends of the manganin are close together, and hence likely to be at the same temperature. In Stein's potentiometer, and in one recently made by the Rubicon Co., the number of coils in the galvanometer circuit was also greatly diminished. The value and significance of these great improvements will be considered presently.

Eliminating Switches

From the beginning of precise thermoelectric work construction alone was almost never relied upon to deal with intrusive thermal forces, but some eliminating switch was also used. With dial-switch resistance difficulties banished, absolutely in Hausrath's three devices, and practically in the Waidner-Wolff and Wenner elements, the eliminating switch, though we have taken it for granted and not thought much about it, is evidently more important than all the other potentiometer improvements of 1907-1910. It eliminates completely all thermal intrusives, though how long their elimination lasts depends on their rates of change. Since, however, the intrusives in coils down in the potentiometer case are small and vary slowly, it is not surprising that the 1907 potentiometer designs, used with eliminating switches, have proved generally satisfactory for 30 years.

Two eliminating methods are well known; one, described by Diesselhorst, reversing both battery and thermel, when the change of deflection is twice the desired reading; the other, described by White, disconnecting both, while substituting a neutral coil for the thermel so as to keep the galvanometer circuit normal. The second method is easier. During the disconnection the galvanometer reading is set to zero, and readings can then be made for some time, as if there were no such thing as intrusives. With reversal, two observations must be made for every important reading, and more if the quantity read is changing. Sometimes this extra demand is serious. If the total intrusive voltage is also changing, the disconnection method remains the better, though its relative superiority is less.

It is claimed that in the reversal method the two readings, right and left, give a double throw, and hence twice the precision of reading. This seems fallacious. With reversal there are two estimations of tenths; with disconnection we have one setting on a line, which has less error. Hence there is only a slight gain to offset the considerable inconvenience.

One good reversal method I have not seen mentioned. Take a deflection; then set to zero; then reverse, and read the double deflection with only one estimation. Here the double precision of reading is really secured, but the method can be readily used only for stationary values, and is somewhat slow.

Wenner's Method

Recently a third elimination method has been brought forward by Wenner.[8] It is a reversal method, but differs in that the reversal is practically instantaneous, the time during which the circuit is either open or shorted being quite inappreciable. The attainment of this feature demands that only one circuit shall be operated upon—the battery may not be reversed. And this demands further that the potentiometer be reversed together with the thermel, which in turn requires the potentiometer to be absolutely and totally neutral.

To say that at the present time the only advantage of the triumphant neutrality of some of the recent potentiometers lies in their making Wenner's type of reversing key usable may be startling, but it can easily be shown to be true. Consider an installation in which the more usual type, either of reversing, or of disconnecting, elimination is used. The total intrusive emf, perhaps mainly in the galvanometer, is likely to reach one microvolt or more. The eliminating switch takes care of this, and while it is doing so can surely take care also of any other intrusive of comparable magnitude—still more surely of smaller ones. If, therefore, the total intrusive in the potentiometer is only as small as 0.1 microvolt, its effect will be insignificant, and any effort spent in making it smaller will be quite wasted, with any usual eliminating switch. Hence validating the Wenner reverser is the only special service left for the very neutral potentiometer to perform.

What, then, is the value of this reverser? As I understand, from an explanation given to me by Dr. Wenner, there are two advantages, each of which amounts to a virtual shortening of the galvanometer period. First, a throw of the galvanometer is avoided. In reading to 0.001 microvolt a deflection of one microvolt is 100 scale divisions, and a deflection of this magnitude may occur with a customary switch if the circuit is opened or shorted. No such swing as that would actually be reached in ordinary work, for such a switch should take only 0.1 second—or less—to throw, while the period of the galvanometer is pretty sure to be over, perhaps much over, 3 seconds. However, the coil will acquire, during the brief open circuit a velocity which, half the time, it must lose before it can begin moving to equilibrium. Hence there will be a virtual increase of the period, which, while not so much as a doubling, will be objectionable to an observer occupied with an exacting task. Wenner's switch avoids this.

The second advantage of the Wenner switch lies in using quick operation to simplify the treatment of a variable intrusive in work of the very highest precision. If the rate of variation of an intrusive should be, as it no doubt sometimes is, rapid enough to demand resetting of zero every 10 minutes when reading to 0.1 microvolt, then in reading to 0.001 microvolt (an approach to which is one object of the Wenner switch-potentiometer combination) the two readings which are compared must not be over 6 seconds apart. This may be less than the period of the galvanometer, and nearly always too close to it. There are several ways out of the difficulty. An attractive one is: If the thermel voltage can be balanced very closely indeed the instantaneous throw of the Wenner switch gives a change of deflection so small that the tail end of it is too small to perceive, and can be neglected; the first and largest part of it will then be completed in a third, perhaps, of the total period of the galvanometer, and the necessary shortening of time thus secured. This method evidently makes the best offering when close balancing is desired for other reasons; since it demands balancing it involves the attendant disadvantages as pointed out in the foregoing discussion of the Lindeck. Hence it is either unsatisfactory or quite inadmissible when the *main* emf is varying appreciably, or for rapid alternating readings. In such cases the Wenner switch can of course be used; but it is used like any other reversing switch. Its advantages now are the very small kick of the galvanometer and the fact that it is on hand whenever the close balancing method can be used.

If the galvanometer zero is adjusted, as recommended by Brooks (*op. cit.*), by using a counter emf, the kick of the galvanometer can be rendered harmless, and the more rapid and convenient disconnection eliminating method can be used without drawback in cases where close balancing is not easy.

Whenever the variation of the intrusive needs to be considered in all measurements, the superiority of the disconnection method over the reversal becomes quite small—utterly inadequate to justify a sacrifice in its favor of Wenner's ingenious method of reversing the negligible deflection, in cases where the latter is likely to have any considerable usefulness. No such painful choice, however, need ever be encountered. It is the simplest thing to insert in almost any potentiometer system having a Wenner switch a disconnection switch also; every single reading can then be made with the switch most desirable for it, with no other special preparation or manipulation than taking hold of the proper switch handle. Such an alternative switch seems highly to be recommended. Even where the method of reversing the balanced deflection is often imperative there will usually be readings or even whole experiments where it is unnecessary or impossible.

The Alliance of Thermel and Double Potentiometer

A friend for whose opinion I have a high regard wishes that this paper might contain some recommendation of the thermel itself. This wish may appropriately be granted, since the thermel was responsible for one important outcome of the development period, 1905-1908, namely, the double potentiometer. This is a potentiometer having two, or even three, sets of dial switches, connected to the same coils, each set capable of being put in or out of action by throwing a switch, the master switch, which also connects an outlet to one or another of several thermels or groups of thermels. Thus, when several different emf's are being watched or followed, the observer can turn from one to the other without resetting—and keeping track of—the dial switches every time. This may be indispensable where frequent readings are to be made, and makes generally for less fatigue and chance of error. The relation of this form of potentiometer to the thermel is that each demands and justifies the other. The performance of one thermel can often be duplicated by the resistance thermometer. Indeed, for the very precise measurement of a single temperature the resistance thermometer is a natural choice. This is not in the least because its precision is any higher; in fact, the most precise of recent calorimetric measurements have been done with thermels. The reason is the moderate inconvenience of taking care of the rear or reference end of the thermel. But this inconvenience ceases to count when the thermel offers advantages in other directions.

Chief among such advantages are greater simplicity where differences of temperature are the direct object of some of the observations; the facility with which thermels can be made; and the rich possibilities of varied temperature observations which they give when combined with the double potentiometer, not only where several readings are almost essential for maximum precision, but also where they offer a gratifying luxury of information about all the temperatures affecting the experiment.

Selector Switches

Given the double potentiometer, which may be highly important, the additional provision for reading more than three thermels adds very little in trouble or expense. The simplest way, which has doubtless been used often without seeming worth description, is to insert copper knife switches in one or more outlets of a White potentiometer. Such switches tend to be highly neutral, if the connections to them are suitably made with fine wires. To change from one thermel to another will take one, two, or three short motions in different cases.

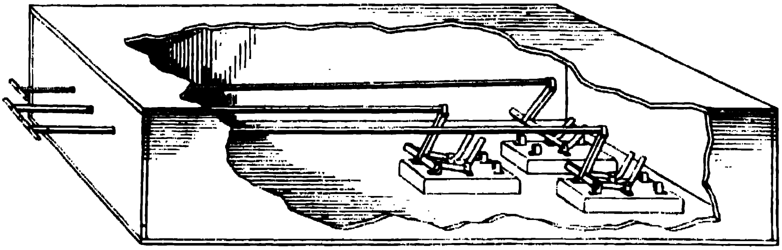

FIG. 8. Perspective of switches, showing double-ended knives, pull-rod connections, and method of working two switches together.

A more advanced arrangement is to have a quadruple knife switch select the dial-switch connection, replacing the master switch of the potentiometer, and then have this and the thermel selector-switch thrown by one motion. Fig. 8 shows an early and crude way of doing this, with the two bars grasped together by the hand.[9] It is better to have a long cross-bar on the rod of the dial selector, which is pushed by a stout pin projecting sideways from the rod of the thermel selector. Through being able to shift the pin so as to contact different bars, any thermel can be instantly associated with any dial combination without having to alter any connections. A compact apparatus on this principle,[10] using pressure contacts instead of knife switches, is shown in Fig. 9. The push rods are held against springs by a locking bar, which is released as any other rod is pushed in; hence every connection is given by a single motion. All contacts must be made with a little wipe. The mechanical parts of such an apparatus were made in about 12 hours, on a first trial. I used one for 15 years.

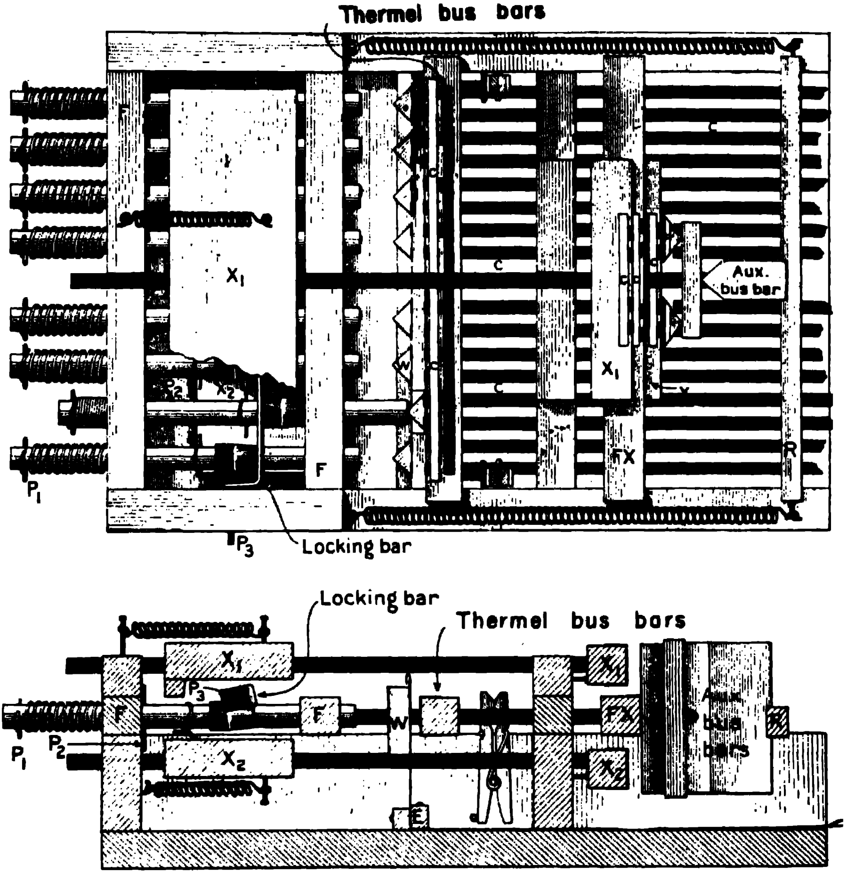

FIG. 9. Ideally convenient selector and master switch. One simple push gives connection to any thermel, together with any desired dial-switch combination.

Those who have never enjoyed a multiple-reading arrangement may perhaps feel that the switches just described are complicated, as compared to the simplicity of just one temperature to read. It is simpler, however, to read temperatures than to calculate or guess at them. And Fig. 9, while it may represent some complication of apparatus, offers a simplification of *manipulation,* which seems more important.

Summary

In 1905 the beginnings of a wide use of thermels led to a demand for potentiometers capable of measuring to 0.1 microvolt, or even somewhat better. The chief obstacle was intrusive electromotive forces, the worst of which came from the switches. By 1908 means, seven in all, had been devised for overcoming this obstacle. The method was not to redesign the switches but to arrange them so that their intrusives did not get into the galvanometer circuit. This greatly eased the burden on the most important device of all, the eliminating switch, which removes the error from all thermal intrusives. A parallel development was two devices for rapid reading, the provision for reading two figures on the galvanometer, and, in reading several thermels along together, a selector switch for the dials which worked together with the one for different thermels.

Twenty or thirty years later potentiometers are being improved so that the intrusives in them are nearly or quite as small as 0.001 microvolt. This improvement is at present of no particular advantage except as it is used to enable Wenner's very rapid eliminating switch to be employed. This switch may often give several times the precision of the older methods, and its special advantage is in the measurement of constant voltages.

Discussion

F. Wenner, National Bureau of Standards: Dr. White has discussed elimination methods, eliminating switches and reversing switches, but his distinctions between a method, that is a general procedure followed in making a measurement, and the apparatus necessary for the use of the method are at times not clear-cut. Apparently he has discussed four methods of reducing the effects of extraneous electromotive forces which for the most part are in the galvanometer branch of the potentiometer.

The first of these methods is comprised of the following operations:

(1) The potentiometer is balanced in the usual way.
(2) The source of the electromotive force being measured is disconnected.
(3) The test current through the potentiometer is reversed in direction.
(4) Connections to source of the electromotive force being measured are closed in the reversed direction.
(5) The potentiometer is again balanced in the usual way.
(6) The average of the two balances of the potentiometer is taken as the true balance, or a correction is determined and applied to a series of balances made in the usual way but before any marked changes occur in the ambient temperature.

The second method is comprised of the following operations:

(1) An approximate balance of the potentiometer is made starting, if necessary, with a reduced sensitivity of the galvanometer.
(2) The source of the electromotive force being measured is disconnected.
(3) The potentiometer current is switched to an auxiliary circuit having a resistance approximately the same as the resistance of the potentiometer.
(4) A neutral coil having approximately the same resistance as the resistance of the source of the electromotive force being measured is connected in the circuit.
(5) The galvanometer scale is so adjusted that the zero of the scale corresponds with the "false zero" of the galvanometer.
(6) The neutral coil is disconnected.

(7) The current is reëstablished in the potentiometer circuit.
(8) The source of the electromotive force being measured is reconnected in the circuit.
(9) A more precise balance of the potentiometer is established (or the lack of balance is read from a deflection of the galvanometer) and used as though there were no extraneous electromotive force.

The third method makes use of a feature common to most procedures in balancing a potentiometer; namely, that when the high-sensitivity key is open the galvanometer circuit is closed through a resistance such as to give a suitable damping of the galvanometer. The method is comprised of the following operations:

(1) An emf is intentionally introduced into the galvanometer circuit and so adjusted that the galvanometer deflection does not change on alternately opening and closing the galvanometer circuit through its damping resistance.
(2) A balance of the potentiometer (or series of balances) is then made in the usual way (or read partially from a deflection of the galvanometer) and used as though there were no extraneous emf.

The fourth method is an adaptation to potentiometer measurements of a method which since about 1912 has been used regularly in the National Bureau of Standards in the testing of precision standard resistors, bridges and potentiometers by bridge methods. It is comprised of the following operations:

(1) An approximate balance of the potentiometer is made in the usual way.
(2) The high-sensitivity key is locked in the closed position.
(3) Successive reversals of connections are made at a point in the circuit such that any emf resulting from a lack of balance of the potentiometer is alternately in one and then in the other direction in the galvanometer branch of the potentiometer. Each reversal is made in a time which is very short relative to the period of the galvanometer, and successive reversals are made at intervals corresponding approximately to the period of the galvanometer. These reversals of connections are continued while the adjustment of the balance of the potentiometer is carried to the refinement desired, or until the observed changes in the deflection of the galvanometer can no longer be associated with the position of the switch serving to make the reversals of connections.
(4) Balances of the potentiometer thus obtained are used as though there were no extraneous emf or other factors affecting the equilibrium position of the galvanometer.

For the use of any of these methods it is necessary to have apparatus at least a part of which is constructed especially for the method selected. With apparatus of equal quality and with equal care in its use under similar conditions, errors from extraneous emf's, and other factors affecting the equilibrium position of the galvanometer with the galvanometer circuit closed, should be expected to be somewhat less with the first, and still less with the fourth, than with either the second or the third method. The relative magnitudes of the errors would be approximately 3 for the first method, 5 for the second method, 5 for the third method and 1 for the fourth method.

If the permissible error is slightly in excess of one microvolt, reasonable care in the design, construction and use of the apparatus in the usual way is all that is required. If the permissible error is 0.1 microvolt, either the second or the third of the methods would be satisfactory, provided reasonable precautions are taken in their use. However, if the permissible error is not in excess of 0.01 microvolt, the required accuracy is not likely to be realized by the use of any of these methods except the fourth, and then only in case the emf being measured remains practically constant for a minute or more, and the apparatus is exceptionally well designed, is exceptionally well constructed and is used by a person appreciating fully the difficulties of precise measurements.

If balances of the potentiometer are to be made to a specified accuracy, such for example as 0.1 microvolt, they can be made in less time and with considerably less effort on the part of the observer by the use of the fourth than by the use of any one of the other three methods. Furthermore a single balance or a relatively small number of balances usually can be made in less time and with less effort on the part of the observer by either the first or the third method than by the second method. If, however, conditions are such that a large number of measurements must be made in a relatively short time, especially if they are to be regularly spaced in time, such for example as every 15 seconds, complete balances of the potentiometer cannot be made, so it is necessary to read lacks of balance from deflections of the galvanometer. Therefore, the second and the third, provided the zero of the galvanometer scale is made to coincide with the "true zero" of the galvanometer, are the only two of the four methods which could be used.

Having well-designed apparatus for the use of the second method, and having constructed a neutral coil of resistance equal to that of the source of emf being measured, operations 2, 3 and 4 are performed by turning a knob in one direction to a stop; and operations 6, 7 and 8 are performed by turning the knob in the opposite direction to another stop. Furthermore, in a series of measurements, the fifth operation need be repeated only occasionally. Likewise, in a series of measurements by the third method, the first operation need be repeated only occasionally. It is for these reasons that successive measurements may be spaced in time about as closely by the second method, which apparently is the more complicated, as by the third method.

J. L. Thomas, National Bureau of Standards: For precise measurements of electrical resistance at the National Bureau of Standards the galvanometer circuits which we use with our bridges are entirely of copper. The galvanometers and connections are shielded against air currents which might cause sudden temperature changes. In spite of all these precautions there is usually a stray electromotive force in a galvanometer circuit of a few tenths of a microvolt, and its magnitude is continually changing. In order to balance to the required accuracy, the galvanometer circuit is left closed, and the bridge is considered balanced when no change in the galvanometer reading results from a reversal of the battery current through the bridge. No effort is made to maintain the galvanometer reading at any particular value when the battery circuit is open. If the stray emf's are not changing too rapidly, a bridge balance corresponding to 0.01 microvolt or better may be obtained, even with the relatively much larger strays which are present.

In the precise measurement of small emf's, even with the remainder of the measuring circuit free from stray emf's, it does not seem possible to reduce the strays in the galvanometer circuit sufficiently so that they may be neglected. Brooks and Spinks introduced in the galvanometer circuit a small emf which could be adjusted so as to exactly balance the stray emf's. This is satisfactory if the strays are constant, but in practice the method is rather tedious as they are continually changing.

In attacking the problem of the strays in the galvanometer circuit of potentiometers, Wenner used the same technique that has been so successful in the case of bridges. He proposed that the galvanometer circuit be left closed and the potentiometer be adjusted until no change in the galvanometer deflection should result when the connections to the potentiometer are reversed. The method does not require one particular type of potentiometer circuit nor does it require the use of the particular type of reversing key which Wenner described. It does, however, seem to be the best method yet described for taking into account the stray emf's in the galvanometer circuit.

I do not mean to imply that the elimination of the effect of the stray emf's in the galvanometer circuit will solve the problem of making accurate measurements of small emf's. It is just as necessary to reduce unwanted emf's from the remainder of the circuit. This can be done by the use of special circuits and by the careful design and careful shielding of the resistance elements and switches. However good the methods may be, the completed potentiometer is no better than the parts that have been constructed to carry out the methods.

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Leakage Control by Shielding

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Measuring System Completely Isolated

Most thermel work is done in rooms where power circuits of 110 volts or higher are used. In the humid weather of summer leakage currents from these circuits can usually be detected flowing over the floor and walls. The general experience has been that the insulation, even of the best apparatus, has been insufficient in summer to prevent such currents from flowing through the measuring system and so through the galvanometer, thus causing a false deflection that is superimposed upon the regular deflection.

These spurious leakage currents can be avoided or minimized by supporting the measuring system on a continuous metal shield. This shield consists of a number of connected metal plates, interposed at every point where any leakage current can enter or leave the measuring system. The current from outside, reaching the shield, flows along it rather than through even poor insulation; hence it does not enter the measuring system at all. The shield furnishes a low-resistance shunt path for the leakage current. Thus the measuring system may be given the same protection as from perfect insulation although the actual insulation may fall far short of perfection. For currents of this sort the air can be taken as a perfect insulator (except within electric furnaces); hence the interposition needs to be made only where there is solid contact, and this will usually call for a few plates of metal connected together by wire. The simplest and most satisfactory case of shielding is illustrated in Fig. 1.

Some of those vagrant currents from power lines, which often abound on the floor and walls in summer, are represented as progressing via the two tables, as shown by the dotted lines. Passing from one table to the other through the measuring system, they affect the galvanometer, in 1a. But in 1b the leaking current strikes the metal plate on top of the first table and then follows the low-resistance path across to the other and so down to the floor, leaving the measuring system entirely unaffected. Nothing but an actual break in the shield can possibly impair the shielding protection in such a case. Such a break may be fatal. It is well, therefore, to construct the shield so that all its parts are in series. The continuity of the whole may then be determined by a single test.

It is evident that the system will nearly always drift to the potential * of the shield, but no thought or attention need be given to that, except with alternating currents. (See page 282.) In some special cases a connection between the two may be desirable, or perhaps undesirable. Whichever it is, and whether the shield should be grounded or not, the experimenter can decide in any case by a little thought. If without thinking he assumes, for example, that the shield should *of course* be grounded, or "earthed," he may be in for trouble. Metal table-legs may be conveniently made a part of the shield. So may be the wires supporting overhead cables.

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* Small potentials generated within the measuring system are ignored here but are discussed later, (see page 283).

Measuring System Directly Connected to Power Supply

In the case just discussed the shield was interposed between the thermel system and its surroundings at all points of contact, and gave its potential to the system. This is impossible when the system is connected to a source of high voltage. The voltage of the system being fixed, the shield must be brought to this potential for avoiding leakage, and a direct connection is essential. For example, if the measurement is of the voltage drop through a coil to determine the current passing through a heater, the shield should be connected to the power line where it meets the coil.[1]

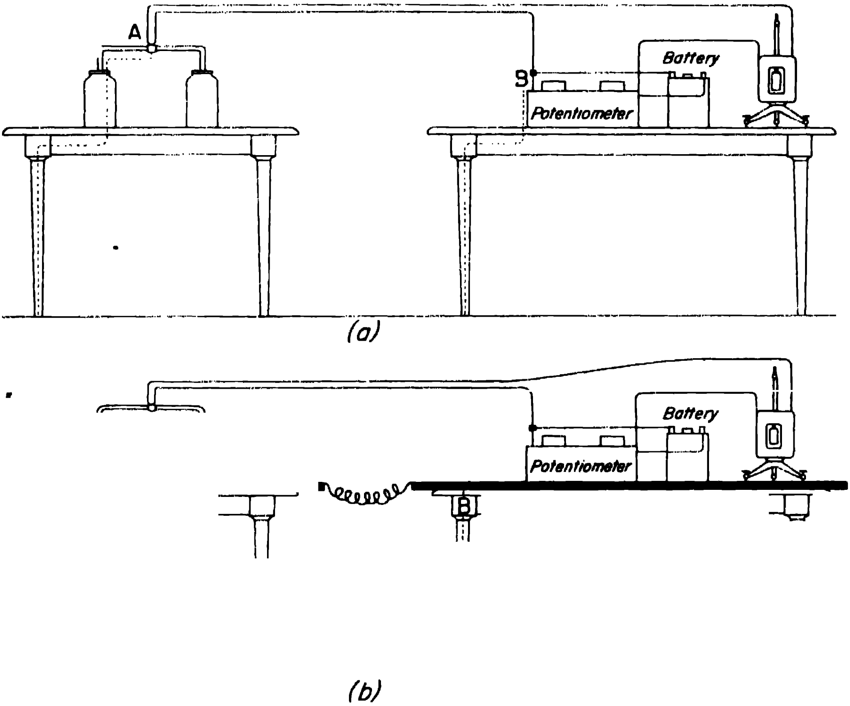

FIG. 1. Diagram showing possible leakage paths in (a) unshielded, (b) shielded, system of apparatus for measuring emf of thermels. By means of the shield the potential available for producing an extraneous current between *A* and *B* is reduced to a negligible amount.

Measuring Emf of Thermels in Electric Furnaces

When a thermel is used to measure high temperatures in an electric furnace, both the hot atmosphere of the furnace and the hot refractory may act as a conductor between the heater and the thermel. There is, however, no definite point of "contact" between the heating coil and the thermel, but a series of points of flow between them, which may differ widely in potential. Hence the preceding method cannot be applied. The most effective shielding for furnace work is to extend the shield into the furnace, giving a shield of the perfectly satisfactory type of Fig. 1, which calls for no direct connection. This actually was done quite early, and no sort of failure with it has yet been reported. The sheath of very thin platinum foil needed to carry the shield down into the furnace will seldom conduct heat at all detrimentally. Frequently the junction, if not already within a conducting enclosure, such as a crucible, will admit of such protection. When it does not, the method still can generally be used. Greig has found that the shielding is complete at very high temperatures with a sheath around the thermel extending from outside the furnace to within about 2 cm. of the tip. Possibly the insulating tubes conducted well enough to perform the function of metal for a short distance.

At high temperatures some contamination of the thermel may arise from a large area of platinum in the furnace and in special cases there are other objections to the sheath. Hence there is considerable usefulness in methods which avoid the use of the sheath and which have been found quite adequate in most cases. One such method is indicated in Fig. 2. In this case the shield, now supported on first-class insulation, is brought to the potential of the measuring system by a direct connection. Currents now flow from the heater through the measuring system and shield to the outside, but are kept at an exceedingly low value by the insulation. Such a current entering the thermel at any point and flowing through the connection to the shield has two paths. By making the connection close to the point at which the current enters the measuring system, the ratio of the resistances of the two paths is kept high, so that only a small fraction of this very small current passes through the galvanometer, which is in the high-resistance path.

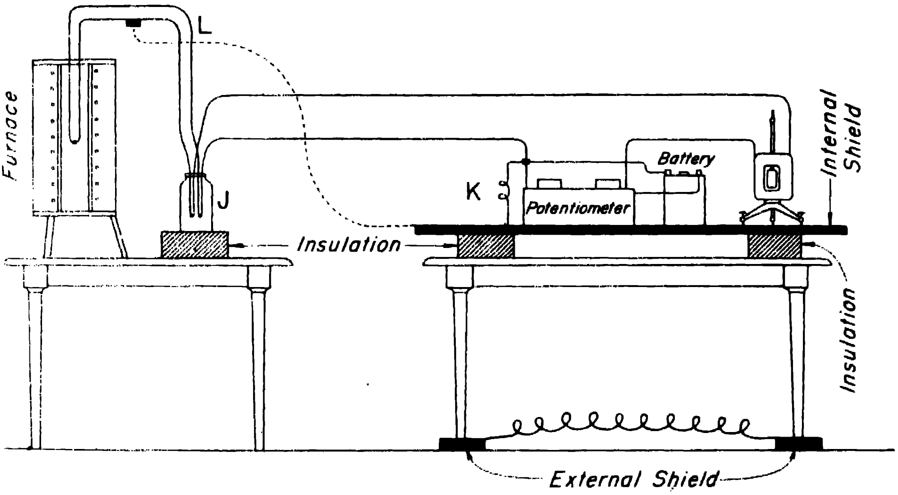

FIG. 2. A useful type of shielding for systems containing a thermel in an electric furnace. The internal and external shields are separated by the best available insulation. Connection between the measuring circuit and the internal shield is effected at *K*. An alternative connection is shown by the dotted line.

In Fig. 2 the dotted line represents a connection of the shield to the thermel circuit at *L* very near the furnace. An alternative connection is at *K*. Unless there is a significant resistance between these two points, the connection at *L* is only a little better than that at *K*, which is the one to use if the internal shield is used for the battery also.* *K* is then in the thermel circuit near one pole of the battery and also near one terminal of the thermel. The reason for the second, here outer, shield is given on page 283.

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* See page 283.

C. N. Fenner connected the shield by a third wire to the junction of the thermel, which of course is usually the hottest part of the thermel and might therefore be assumed to be the point at which the most of the leakage enters the system.

The potential across the insulation between the two shields may be kept low, and the leakage through it therefore small, by a device that J. W. Greig and H. S. Roberts of the Geophysical Laboratory have used in some of their work. A sliding-contact voltage divider is installed as a shunt to the heater of the furnace; the slider is connected to the outer shield, and by adjusting the slider its potential is brought close to that of the thermel in the furnace.

These methods, involving connection to the shield, have usually given satisfactory shielding, but do not invariably do so. For this the following explanation suggests itself. With both air and solids conducting inside the hot furnace, and the heating coil setting up a large difference of potential, there may be considerable flows within the thermel in the furnace. A rather large voltage is back of these currents. Asymmetry in them might easily cause a residual current out through one thermel wire and back through the other. Where such currents exist, this type of shielding may not give complete protection from leakage error. In some instances it may be necessary to employ the first method described for use with thermels.

Alternating Current

Our shielding technic was originally developed under a regime of direct-current power lines; now alternating current is generally used. It might be supposed that with the furnace running on alternating current any leakage currents would be alternating, and therefore would not cause an observable deflection of the galvanometer, but this is not so. There is a demonstrated rectifying effect in the furnace, possibly as low as 900°.

Another effect is well established. With alternating current and perfect shielding, when there is no leakage current through the galvanometer, there may be an alternating charging of the system, which causes an electrostatic attraction between the galvanometer coil and the insulated pole-faces, causing a deflection which is always in the same direction, depending on the asymmetry of the position of the coil. The remedy, which does also for electrostatic charging in winter, is to connect the coil to the poles. This might be classified as shielding, with the poles as shield.

An alternating leakage current through the galvanometer, though it causes no steady deflection, may cause a series of slight alternating ones, making the mirror image fuzzy. This is better in one respect than the deflection with direct current, in that one cannot help seeing that it is there, and so one does not unwittingly record a false deflection. If it causes loss of precision, it is amenable to the same treatment as for direct current.

Insulation and Double Shielding

The insulation of a shield is done with comparatively few blocks of insulating material, whose mechanical requirements are of the simplest, and which can easily be renewed or cleaned. Hence, as far as external leakage is concerned, it will somewhat improve the original insulation of even the best systems. Especially advantageous is the chance easily to use paraffin, for paraffin has the valuable property of being largely, if not absolutely, indifferent to dampness. Paraffin may contain water, without doubt, but that does not affect its insulating power, even in very moist air.

The outer shield, as shown in Fig. 2, is of considerable help in maintaining effective insulation. (1) It enables the entire insulation to be tested at once by measuring the insulation resistance between the two shields. (2) For measurements other than in the furnace, which fall into the type of Fig. 1, where high shield insulation is usually not important, the outer shield can be extended under the apparatus concerned, and the inner shield, with its more exacting insulation, can be confined to furnace work, and to protection against leakage from the "bull cell."

In Fig. 2, if the Thermos bottle, *J*, for the cold junction stands on the best kind of insulation, there may be some advantage in not running the internal shield under it. As it stands, leakage through the bottle has two characteristics; it comes from near the furnace, and it is blocked by excellent insulation, and in these respects it is identical with leakage through *K*. On the other hand, if the insulation under the bottle happens to be a little inferior to the other, its effect will now be confined to the bottle leakage, while a connection to the shield would extend the detriment to the entire shield. Finally, there is the possible disadvantage of extending over to the perhaps crowded neighborhood of the furnace the shield which needs the best insulation throughout its extent. With Greig and Roberts' method (page 282) both shields should be under the Thermos bottle.

It is often advantageous, and little trouble, to have the "bull cell" (measuring current battery) supported on the insulated shield, which is connected to the potentiometer near one end of the battery at *K* (see Fig. 2), because detrimental leakage at 2 volts is not impossible. Special insulation between the battery and the shield is not necessary, since leakage will simply go back along the shield to the other pole of the battery.

Acknowledgment

Grateful acknowledgment is made to L. H. Adams and J. W. Greig for helpful criticisms.

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Methods of Testing Thermocouples and Thermocouple Materials

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I. Introduction

Methods of testing thermocouples and thermocouple materials have been developed to supply the need of those industries to which the measurement and control of temperature are essential. The recognition by the various industries in this country that the measurement and control of these temperatures are essential to a uniformly high quality of product has led, in recent years, to a tremendous increase in the use of temperature-measuring equipment. Where the higher temperatures are involved by far the large portion of such measurements are made with thermocouples, and therefore these devices must be regarded as one of the important tools of modern industry.

The users of thermoelectric pyrometers have been demanding ever-increasing accuracy in these instruments. Thermocouple materials are being bought on closer specifications and the pyrometer manufacturers have been setting up smaller tolerances in the inspection and calibration of their product, with the result that practically all pyrometric equipment now being sold is of very high quality. Reliable methods of testing thermocouples and thermocouple materials are required to realize the degree of accuracy now demanded. The purpose of this paper is to describe the more important of these methods and to point out certain precautions that must be observed to secure reliable results. The essential features of many of these methods and much of the apparatus described here have been devised and described in whole or in part by various writers, but references to their papers will be made only when it is felt that a more detailed description than we have given will be helpful to the reader.

Combinations of metals and alloys extensively used in thermocouples for the measurement of temperatures in this country are listed in Table 1, together with the temperature ranges in which they are generally used and the maximum temperatures at which they can be used for short periods. The period of usefulness at high temperatures depends largely upon the temperature and the diameter of the wires. The methods described in this paper were devised primarily for calibrating couples in the usual temperature ranges, but unless otherwise indicated they may be used up to the maximum temperatures at which the various types of couples can be used.

Table 1. Types of Thermocouples and Temperature Ranges in Which They Are Used.

	Usual temperature ranges		Maximum temperatures	
Type	(°C)	(°F)	(°C)	(°F)
Platinum-rhodium	0 to 1450	0 to 2650	1700	3100
Chromel-alumel	- 200 to 1200	- 300 to 2200	1350	2450
Iron-constantan	- 200 to 750	- 300 to 1400	1000	1800
Copper-constantan	- 200 to 300	- 300 to 570	600	1100

II. General Considerations

1. Temperature Scale

The object in the calibration of any thermocouple is to determine an emf-temperature relation in which the temperature is expressed on a definite and reproducible scale. The International Temperature Scale,[1] adopted in 1927 by thirty-one nations, is now in practically universal use. The methods of realizing this scale are described in detail in the reference cited. The instruments, calibration points, and interpolation equations to be used in the various ranges of the scale are summarized in Table 2.

2. General Methods

In order to calibrate thermocouples to yield temperatures on the International Scale, it is apparent from the definition that they must be so calibrated that their indications agree with those of the platinum-resistance thermometer in the range −190 to 660 °C, the platinum-10 per cent rhodium thermocouple in the range 660 to 1063 °C, and the optical pyrometer above 1063 °C. The most direct procedure would therefore be to compare the couples directly with these primary instruments in the appropriate temperature ranges. However, to follow such a procedure in the calibration of every couple requires more time and apparatus than is justifiable or necessary since, in most cases, other methods are available which yield results sufficiently accurate. For example, a thermocouple may be compared indirectly with any of the primary instruments by determining its emf at a number of fixed points, either those which are used in defining the scale or others, the values for which have been determined with the primary instruments. If a few laboratories maintain the apparatus necessary to calibrate thermocouples as working standards to yield temperatures on the International Scale, these standards may be used subsequently to calibrate other couples. This procedure is used far more than any other because the comparison of the indications of two couples is usually simpler than the comparison of two different types of instruments.

The temperature-emf relation of a homogeneous * thermocouple is a definite physical property and therefore does not depend upon the details of the apparatus or method employed in determining this relation. Consequently, there are innumerable methods of calibrating thermocouples, the choice of which depends upon the type of couple, temperature range, accuracy required, size of wires, apparatus available, and personal preference.

Thermocouple calibrations are required with various degrees of accuracy ranging from 0.01 to 10 or 20 °C. For an accuracy of 0.1 °C agreement with the International Temperature Scale and methods of interpolating between the calibration points become problems of prime importance, but for an accuracy of about 10 °C comparatively simple methods of calibration will usually suffice. The most accurate calibrations in the range −190 to 300 °C are made by comparing the couples directly with a standard platinum-resistance thermometer in a stirred liquid bath. In the range 300 to 660 °C (and below if a platinum-resistance thermometer or stirred liquid bath is not available) couples are most accurately calibrated at the freezing or boiling points of pure substances. Between 660 and 1063 °C, the platinum-10 per cent rhodium thermocouple calibrated at the freezing points of gold, silver, and antimony, serves to define the International Temperature Scale and other types of couples are most accurately calibrated in this range by direct

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* A homogeneous thermocouple is one in which each element is homogeneous, in both chemical composition and physical condition, throughout its length.

Table 2. Instruments, Calibration Points, and Interpolation Equations of International Temperature Scale.

—Temperature range—		Instrument	-Calibration points (values for pressure of one standard atmosphere)			Interpolation equations[a]
(°C)	(°F)		Fixed point	°C		
-190 to 0	-310 to 32	Platinum resistance thermometer	Boiling point of oxygen	-182.97	-297.35	$R_t = R_0[1 + At + Bt^2 + C(t-100)t^3]$
			Melting point of ice	0.000	32.000	
			Boiling point of water	100.000	212.000	
			Melting point of sulfur	444.60	832.28	
0 to 660	32 to 1220	Platinum resistance thermometer	Melting point of ice	0.000	32.000	$R_t = R_0(1 + At + Bt^2)$
			Boiling point of water	100.000	212.000	
			Boiling point of sulfur	444.60	832.28	
660 to 1063	1220 to 1945	Platinum to platinum 10% rhodium thermocouple	Freezing point of antimony	[b](630.5)	[b](1166.9)	$e = a + bt + ct^2$
			Freezing point of silver	960.5	1760.9	
			Freezing point of gold	1063.0	1945.4	
1063 and above	1945 and above	Optical pyrometer	Freezing point of gold	1063.0	1945.4	$\log_e \frac{J_2}{J_1} = \frac{C_2}{\lambda}\left(\frac{1}{1336} - \frac{1}{t+273}\right)$

[a] R_t is the resistance at t° C, R_0, the resistance at 0 °C; A and B are constants determined by calibration at the boiling points of water and sulfur, and C is an additional constant determined by calibration at the boiling point of oxygen. e is the emf at t° C and a, b, and c are constants. J_2 is the monochromatic visible radiation at wave length λ cm emitted by a black body at temperature t° C, J_1 the radiation of the same wave-length emitted by a black body at the gold point, and C_2 is 1.432 cm degrees.

[b] The value for the freezing point of the particular lot of antimony used is determined by means of the platinum-resistance thermometer.

comparison with the standard couple calibrated as specified. Other couples may be calibrated just as accurately at the fixed points as the 10-per cent rhodium couple, but interpolated values at intermediate points may depart slightly from the International Scale. Above 1063 °C, the most basic calibrations are made by observing the emf when one junction of the couple is in a blackbody furnace, the temperature of which is measured with an optical pyrometer. However, the difficulties encountered in bringing a blackbody furnace to a uniform temperature make the direct comparison of these two types of instruments by no means a simple matter. Other methods of calibrating a couple above 1063° C are given under "Melting points" and under "Methods of interpolation."

Although the 10-per cent rhodium couple serves to define the scale only in the range 600 to 1063 °C, this type of couple calibrated at fixed points is used extensively both above and below this range as a working standard in the calibration of other thermocouples. For most industrial purposes a calibration accurate to 2 or 3 °C in the range room temperature to 1200 °C is sufficient. Other couples can be calibrated by comparison with such working standards almost as accurately as the calibration of the standard is known. However, it might be pointed out that outside the range 660 to 1063 °C any type of couple suitable for the purpose, and calibrated to agree with the resistance thermometer or optical pyrometer in their respective ranges, has as much claim to yielding temperatures on the International Scale as the platinum-10 per cent rhodium couple. In fact, at the lower temperatures certain types of base-metal couples are definitely better adapted for precise measurements.

The calibration of couples then may be divided into two general classes, depending upon the method of determining the temperature of the measuring junction, (1) calibration at fixed points and (2) calibration by comparison with standard instruments such as thermocouples, resistance thermometers, etc.

In order to obtain the high accuracies referred to above and usually associated with calibrations at fixed points, it is necessary to follow certain prescribed methods and to take the special precautions described in detail in the following sections, but for an accuracy of about 5 °C the more elaborate apparatus to be described need not be employed.

3. Homogeneity

The magnitude of the emf developed by a couple depends upon the composition of the wires in the region of temperature gradients. The emf developed by an inhomogeneous couple is characteristic of the temperature of the hot junction only when the region of inhomogeneity is not in a region of temperature gradients. Therefore, in order to obtain a high degree of accuracy with a couple, the homogeneity of the wires must be established.

Thermocouple wire now being produced by the wire manufacturers in this country is sufficiently homogeneous in chemical composition for most purposes. Occasionally inhomogeneity in a couple may be traced to the manufacturer, but such cases are rare. More often it is introduced in the wires during tests or use. It usually is not necessary, therefore, to examine new thermocouples for inhomogeneity, but thermocouples that have been used for some time should be so examined before an accurate calibration is attempted.

While rather simple methods are available for detecting thermoelectric inhomogeneity, no satisfactory method has been devised for quantitatively determining it or the resulting errors in the measurement of temperatures. Abrupt changes in the thermoelectric power may be detected by connecting the two ends of the wire to a sensitive galvanometer and slowly moving a source of heat, such as a bunsen burner or small electric furnace, along the wire. This method is not satisfactory for detecting gradual changes in the thermoelectric power along the length of the wire. Inhomogeneity of this nature may be detected by doubling the wire and inserting it to various depths in a uniformly heated furnace, the two ends of the wire being connected to a galvanometer as before. If, for example, the doubled end of the wire is immersed 25 cm in a furnace with a sharp temperature gradient so that two points on the wire 50 cm apart are in the temperature gradient, the emf determined with the galvanometer is a measure of the difference in the thermoelectric properties of the wire at these two points.

After reasonable homogeneity of one sample of wire has been established, it may be used in testing the homogeneity of similar wires by welding the two together and inserting the junction into a heated furnace. The resulting emf at various depths of immersion may be measured by any convenient method. Other similar methods have been described for detecting inhomogeneity.[2]

Tests such as those described above will indicate the uncertainty in temperature measurements due to inhomogeneity in the wires. For example, if a difference in emf of 10 microvolts (abbreviated hereafter μv) is detected along either element of a platinum-rhodium couple by heating various parts of the wire to 600 °C, measurements made with it are subject to an uncertainty of the order of 1° at 600 °C or of 2° at 1200 °C. Similarly, if an emf of 10 μv is detected along an element of a base-metal couple with a source of heat at 100 °C, measurements made with it are subject to an uncertainty of the order of 0.2 °C at this temperature. The effects of inhomogeneity in both wires may be either additive or subtractive and, as the emf developed along an inhomogeneous wire depends upon the temperature distribution, it is evident that corrections for inhomogeneity are impracticable if not impossible.

4. Annealing

Practically all base-metal thermocouple wire produced in this country is annealed or given a "stabilizing heat treatment" by the manufacturer. Such treatment is generally considered sufficient, and seldom is it found advisable to further anneal the wire before testing.

Although the new platinum-rhodium thermocouple wire as sold by some manufacturers is already annealed, it has become regular practice in many laboratories to anneal or "stabilize" all platinum-rhodium couples, whether new or previously used, before attempting an accurate calibration. This is usually accomplished by heating the wire electrically in air. The entire length of wire is supported between two binding posts, which should be close together so that the tension in the wires and stretching while hot are kept at a minimum. The temperature of the wire is most conveniently determined with an optical pyrometer.* It is necessary, however, to add a correction to the observed apparent temperature to obtain the true temperature, which is always the higher. The correction (based on an emissivity of 0.33) amounts to 130 and 145 °C, respectively, for apparent temperatures of 1270 and 1350 °C.

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* The ordinary portable type of optical pyrometer is very satisfactory for this purpose. As commonly used the magnification is too low for sighting upon an object as small as the wires of rare-metal couples, but this is easily remedied by inserting an additional piece of telescoping tubing so that the objective lens of the pyrometer is about twice as far from the pyrometer lamp as it is when sighting upon distant objects. Such a tube should preferably be made of metal, but one made by simply rolling up a sheet of heavy paper will do very well.

There is some question as to the optimum temperature or length of time at which such couples should be annealed to produce the most constant characteristics in later use. As a matter of fact, there is some question as to whether annealing for more than a few minutes is harmful or beneficial. Most of the mechanical strains are relieved during the first few minutes of heating at 1400 to 1500 °C, but it has been claimed that the changes in the thermal emf of a couple in later use will be smaller if the wires are heated for several hours before calibration and use. The principal objection to annealing thermocouples for a long time at high temperatures, aside from the changes in emf taking place, is that the wires are weakened mechanically as a result of crystal growth. Previous to January 1935 the practice at the National Bureau of Standards was to anneal all platinum-rhodium couples electrically for 6 hours at 1500 °C before calibration. The emf of a number of new thermocouples was determined both after annealing for 5 minutes and for 6 hours at 1500 °C and in no case did the change in emf correspond to as much as 2 °C at 1200 °C. After 6 hours of heating, the wires, particularly the platinum element, become much softer. It has been found, however, that annealing at temperatures much above 1500 °C produces rapid changes in the emf and leaves the wire very weak mechanically. The National Bureau of Standards on January 2, 1935, adopted the procedure of annealing all platinum-rhodium couples for 1 hour at 1450 °C.

It has not been demonstrated conclusively that platinum-rhodium thermocouples after contamination can be materially improved in homogeneity by prolonged heating in air, although it is logical to suppose that certain impurities can be driven off or, through oxidation, rendered less detrimental.

5. Instruments

One of the factors in the accuracy of the calibration of a thermocouple is the accuracy of the instrument used to measure the emf. Fortunately, in most instances, an instrument is available whose performance is such that the accuracy of the calibration need not be limited by the accuracy of the emf measurements. For work of the highest accuracy it is advisable to use a potentiometer of the type designed by Diesselhorst,[3] White,[4] or Wenner,[5] in which there are no slide wires and in which all the settings are made by means of dial switches. However, for most work, in which an accuracy of 5 μv will suffice, slide-wire potentiometers of the laboratory type are sufficiently accurate. Portable potentiometers accurate within 40 to 100 μv are also available. Aside from the greater sensitivity obtained, an important advantage of using a potentiometer is the fact that the reading obtained is independent of the resistance of the couple.

Indicators of the galvanometric type are seldom used in making calibrations. Galvanometer indicators should be graduated for a specified external resistance of couple and leads, and the resistance of the indicator itself should be high in order to minimize the effects of changes in the resistance of the couple and leads. Detailed discussion is given and special instruments used in measuring the emf of thermocouples are described in Bureau of Standards Technologic Paper T170.

III. Calibration at Fixed Points

One of the important applications of the method of calibrating thermocouples at fixed points is found in the calibration of platinum-10-per cent rhodium thermocouples to realize the International Temperature Scale in the range 660 to 1063 °C. From such a calibration, together with methods of extrapolation described later, the temperature-emf relation of this type of couple may be determined with an accuracy of about 2 °C at 1500 °C. Calibration at a few other selected points below 660 °C will yield a working standard which is accurate to a few tenths of a degree in the range 0 to 1100 °C. Fixed points are also conveniently used with various degrees of accuracy ranging from 0.1 to 5 °C in the calibration and checking of various types of thermocouples in the range −190 °C to the melting point of platinum (1773 °C). The fixed points for which values have been assigned or determined accurately and at which it has been found convenient to calibrate thermocouples are given in Table 3. The values in the table apply for a pressure of one standard atmosphere (760 mm of Hg) and the variations of the boiling temperatures with pressure are given in the last column

Table 3. Fixed Points Available for Calibrating Thermocouples.

Thermometric fixed point	Values on the International Temperature Scale				Temperature of equilibrium (t_p) in °C as a function of the pressure (p) between 680 and 780 mm of Hg
	Assigned (Primary points)		Determined (Secondary points)		
	°C	°F	°C	°F	
Boiling point of oxygen	−182.97	−297.35			$t_p = t_{760} + 0.0126(p-760) - 0.0000065(p-760)^2$
Sublimation point of carbon dioxide.			−78.5	−109.3	$t_p = t_{760} + 0.1443(t_p + 273.2)\log\left(\frac{p}{760}\right)$
Freezing point of mercury			−38.87	−37.97	
Melting point of ice	0.000	32.000			
Boiling point of water	100.000	212.000			$t_p = t_{760} + 0.0367(p-760) - 0.000023(p-760)^2$
Boiling point of naphthalene			217.96	424.33	$t_p = t_{760} + 0.208(t_p + 273.2)\log\left(\frac{p}{760}\right)$
Freezing point of tin [1]			231.9	449.4	
Boiling point of benzophenone			305.9	582.6	$t_p = t_{760} + 0.194(t_p + 273.2)\log\left(\frac{p}{760}\right)$
Freezing point of cadmium			320.9	609.6	
Freezing point of lead [1]			327.3_6	621.2_5	
Freezing point of zinc [1]			419.5	787.1	
Boiling point of sulfur	444.60	832.28			$t_p = t_{760} + 0.0909(p-760) - 0.000048(p-760)^2$
Freezing point of antimony			630.5	1166.9	
Freezing point of aluminum [1]			660.1_5	1220.2_7	
Freezing point of Cu-Ag eutectic alloy.[2]			778.8	1433.8	
Freezing point of silver	960.5	1760.9			
Freezing point of gold	1063.0	1945.4			
Freezing point of copper [1]			1083.0	1981.4	
Melting point of palladium			1555	2831	
Melting point of platinum			1773	3223	

[1] Standard samples of these materials are procurable from the National Bureau of Standards with certificates giving the freezing point of the particular lot of metal. The values given in this table for these materials apply for the standard samples that are being issued as of the present date.

[2] 28.1% copper and 71.9% silver by weight.

In selecting the points at which to calibrate a couple, one sometimes has a choice between a boiling or a freezing point,* as for example, between the boiling point of sulfur (444.60 °C) and the freezing point of zinc (419.5 °C), between the boiling point of naphthalene (217.96 °C) and the freezing point of tin (231.9 °C), or between the boiling point of benzophenone (305.9 °C) and the freezing point of cadmium (320.9 °C) or lead (327.35 °C). In determining the emf of a couple at a freezing point, the time in which observations may be taken is limited to the period of freezing, after which the material must be melted again before taking further observations. In the case of boiling points, there is no such limit in time since the material can be boiled continuously. In addition there is sometimes a question as to the beginning and end of the interval of constant-temperature characteristic of freezing. On the other hand, it is not necessary to observe the pressure during freezing and in general simpler apparatus and less skill are required to obtain a given accuracy with freezing points.

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* In this paper "boiling point" is used for the temperature of equilibrium between the liquid and vapor phases although the point is usually realized experimentally by immersing the couple in the condensing vapor. "Freezing point" is used for the temperature of equilibrium between the solid and liquid phases when the point is realized experimentally by immersing the couple in the freezing material, and "melting point" is used for the same point when it is realized experimentally by determining the emf of a couple while the material is melting. When conditions permit a choice, freezing points are preferable to melting points of metals because the molten metal can be brought to a uniform temperature just prior to freezing by stirring more easily than the solid can be brought to a uniform temperature just prior to melting, a condition that must be met to obtain accurate results.

1. Freezing Points

The emf developed by a homogeneous thermocouple at the freezing point of a metal is constant and reproducible if all of the following conditions are fulfilled: (1) the couple is protected from contamination; (2) the couple is immersed in the freezing-point sample sufficiently far to eliminate heating or cooling of the junction by heat flow along the wires and protection tube; (3) the reference junctions are maintained at a constant and reproducible temperature; (4) the freezing-point sample is pure; and (5) the metal is maintained at essentially a uniform temperature during freezing. The methods of obtaining these conditions are subject to a choice. However, the essential features of the methods employed at the National Bureau of Standards are described here.

(a) Protection Tubes. Closed-end porcelain or "Pyrex" tubes are generally used to protect thermocouples from contamination, which usually results from the thermocouple wires coming in contact with other metals or metallic vapors or from the action of reducing gases at high temperatures. In the latter case, the silica of the insulating or protecting tube is reduced to silicon which alloys with the thermocouple wires. For temperatures above 600 °C the wires should be insulated by porcelain tubing and protected from contamination by a glazed porcelain tube. It is advisable to heat these tubes before use, to about 1200 °C in an oxidizing atmosphere to burn out any carbonaceous material that may have collected in them during storage and shipping. Protection tubes 5 mm inside diameter, 7 mm outside diameter, and 50 cm long are convenient for platinum-rhodium thermocouples insulated by two-hole insulating tubes 50 cm long and 4 mm in diameter with 1 mm holes. For temperatures below 600 °C, "Pyrex" tubes are very satisfactory for both protecting and insulating the wires.

(b) Depth of Immersion. The depth of the immersion necessary to avoid heating or cooling of the junction by heat flow along the thermocouple wires and protection tube depends upon the material and size of the wires, the dimensions of the insulating and protecting tubes, and the difference between the temperature of the freezing-point sample and that of the furnace and atmosphere immediately above it. The safest method of determining whether the depth of immersion is sufficient is by trial. It should be such that during the period of freezing the thermocouple can be lowered or raised at least 1 cm from its normal position without altering the indicated emf by as much as the allowable uncertainty in the calibration. For platinum-rhodium thermocouples in the protection tube described above, a depth of 10 cm, which is greater than necessary, is used at the National Bureau of Standards.

(c) Reference-junction Temperature Control. The temperature of the reference junctions is most easily controlled at a known temperature by placing them in an ice bath. A wide-mouth thermos bottle filled with shaved ice saturated with water is very satisfactory. Electrical connection between a thermocouple wire and a copper lead wire is easily made by inserting them into a small glass tube containing a few drops of mercury. The glass tubes are then inserted into the ice bath to a depth of about 10 cm. The lead wires should be insulated from the thermocouple wires, except where they make contact through the mercury. The glass tubes should be kept clean and dry inside. Moisture is likely to condense in the tube from the atmosphere but should not be allowed to accumulate. A little moisture and dirt at the bottom of the tube will form a galvanic cell which may vitiate the readings. A later section deals with cold-junction temperatures in general.

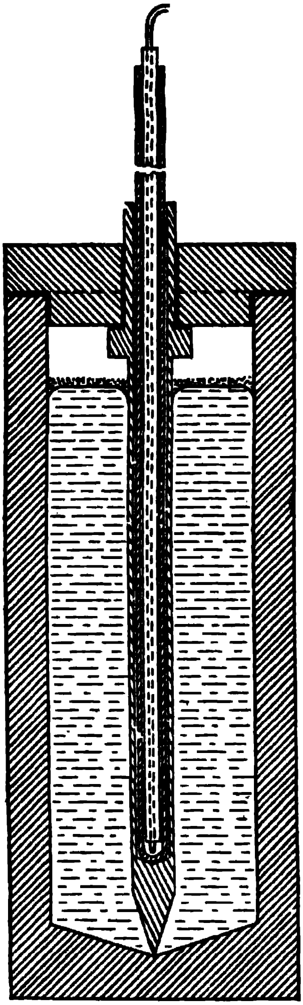

Fig. 1.

Arrangement for protecting a thermocouple in molten aluminum.

(d) Purity of Freezing-point Samples. The temperature at which a metal freezes depends upon the amount and kind of impurities present. The values in Table 3 apply for metals, the purity of which is of the order of 99.99 per cent. The freezing temperature of silver, gold, or copper may be lowered by as much as 0.1 °C and that of antimony, aluminum, zinc, lead, cadmium, tin, or mercury by as much as 0.05 °C by 0.01 per cent of impurities. The purity of the standard-sample freezing-point materials issued by the National Bureau of Standards is not of great importance, as a certificate is issued with each sample giving the freezing temperature determined on that particular lot of metal. However, the purest metals available are selected for these standard samples because a high degree of purity is necessary in order that the metal may give a flat freezing curve.

(e) Crucibles. Of the crucible materials ordinarily used Acheson graphite has the greatest utility and is used almost exclusively at the National Bureau of Standards for this work. It is very pure, can be machined into any desired shape, and can be used in contact with any of the freezing-point materials in Table 3 without detectable contamination of the metals. At high temperatures the gases formed from its oxidation provide the reducing atmosphere usually necessary for the protection of the freezing-point metal. Copper and copper oxide form a eutectic which melts about 20 °C lower than pure copper, and it is possible for molten silver to absorb enough oxygen from the air to lower its freezing point as much as 10 °C. Therefore, copper and silver must be protected from oxygen, and it is advisable also to protect aluminum and antimony from oxygen. This is done by using graphite crucibles with covers of the same material and as an added precaution these freezing-point metals are covered with powdered graphite or charcoal.

Porcelain tubes or crucibles, or any material containing silica cannot be used in contact with aluminum, as the silica is readily attacked. Aluminum is melted in a graphite crucible and the porcelain protecting tube separated from the aluminum by a very thin sheath of graphite. Fig. 1 illustrates one convenient manner in which the sheath may be mounted in the crucible. The sheath is held down in the metal by the weight of the cover and is allowed to remain in the crucible after the aluminum is frozen. The thermocouple protecting tube fits snugly inside the sheath. At the National Bureau of Standards the graphite crucibles used for gold, silver, antimony, and zinc are 3 cm inside diameter and 15 cm deep. The crucibles used for copper, aluminum, lead, and tin are 5 cm inside diameter and 15 cm deep. Porcelain, silica, clay, clay graphite, and "Pyrex" are also used as crucible materials. The latter is very suitable for mercury.

(f) Furnaces. Fig. 2 shows the type of furnace used in the freezing-point determinations. The heating element in No. 6 or 8 gage nickel(80)-chromium (20) wire wound on an alundum tube and imbedded in alundum cement. The space between the heating element and the outside wall is filled with silocel powder. Acheson-graphite diaphragms are placed above the crucible in order to minimize the oxidation of the crucibles and to promote temperature uniformity in the metal.

(g) Procedure. In the calibration of a thermocouple at freezing points, the couple, properly protected, is slowly immersed in the molten metal. The metal is brought to essentially a uniform temperature at the beginning of freezing by holding its temperature constant at about 10 °C above the freezing point for several minutes and then cooling slowly, or by stirring the metal with the thermocouple protection tube just before freezing begins. The emf of the couple is observed at regular intervals of time. These values are plotted and the emf corresponding to the flat portion of the cooling curve is the emf at the freezing point of the metal.

Antimony and tin have a marked tendency to undercool before freezing, but the undercooling will not be excessive if the liquid metal is stirred.

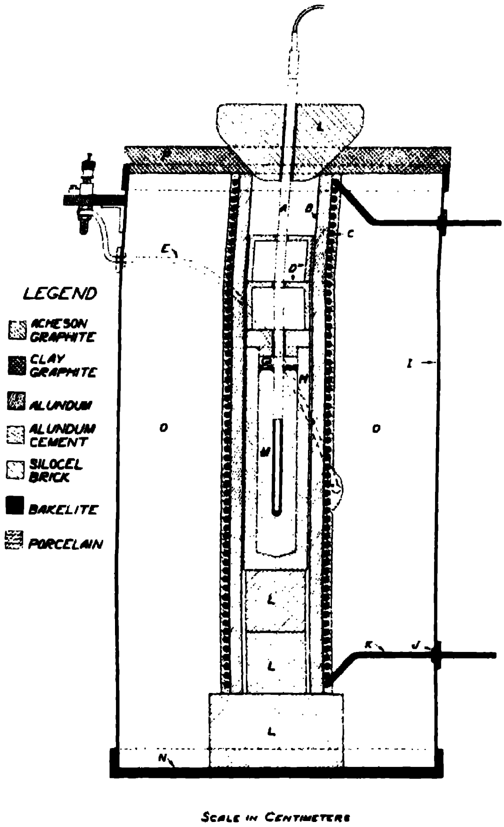

FIG. 2.

Furnace used in calibrating couples at freezing points of metal. A, porcelain protecting tube; B, Alundum furnace tube; C, heating element (80 nickel, 20 chromium); D, graphite diaphragms; E, control thermocouple (chromel-alumel); G, graphite powder; H, graphite crucible; I, sheet steel; M, freezing-point metal; N, cast-iron base; O, silocel-powder insulation.

2. Melting Points

The emf of a thermocouple at the melting point of a metal may be obtained in the same manner and with the same apparatus as that just described for freezing points, but the latter are found to be more satisfactory. However, melting points are used to advantage when only a limited amount of material is available. One method of obtaining the emf of a couple at a melting point with a small amount of material is the wire method.[6] In this method the thermocouple wires are placed in a two-hole insulating tube and a short length of the melting-point sample in the form of wire about the same diameter as the couple elements, is welded between the hot junction ends of the two wires. The dimensions of the melting-point sample are not critical, but there should be at least 1 mm of wire between the two welds. In order that the melting-point sample shall not break before the melting point is reached, the weld should be made and the thermocouple placed in the furnace so that there is a minimum of strain on the melting-point sample. The hot junction end of the couple with the melting-point sample, is placed in a uniformly heated section of a furnace and the temperature increased very slowly as the melting point is approached. When the sample reaches its melting point, its temperature and consequently the emf of the couple remains constant for a fraction of a minute (varying with the rate of temperature rise). After melting is complete, the temperature of the wire and the emf may rise somewhat before the circuit is broken by the separation of the molten metal. The value of the emf corresponding to the melting point is, therefore, the value at the halt in the emf rise and is obtained by continuous observation of the emf as melting is approached or by plotting time versus emf.

The metal most often used in the calibration of couples by the wire method is gold and it has been demonstrated that results can be obtained which are in agreement with those obtained with a crucible of freezing gold to a few tenths of a degree. The same method has been used with palladium but with much less satisfactory results because of electric leakage through the refractory insulation at high temperatures and the oxidation of the palladium. This method is not well adapted to metals which oxidize rapidly, and if used with materials whose melting temperature is altered by the oxide, the metal should be melted in a neutral atmosphere.

If very accurate observations of the emf are not required, the emf at the instant the circuit is broken may be taken, but if this is done the couple should be withdrawn from the furnace immediately and the sample examined to see whether the circuit was broken by the sample melting or by strain on it before melting occurred.

It is not necessary to weld the wire between the thermocouple elements, as fairly good results may be obtained by wrapping a small amount of the wire around the junction. This practice is often applied to base-metal couples by wrapping wires of tin, lead, zinc, or aluminum around the hot junction and heating it until a halt is observed in the heating curve.

One method of checking platinum-rhodium couples at the highest possible point is by heating the junction of the couple until the platinum wire melts. To avoid electric leakage the insulating tube is withdrawn to the colder parts of the heating device leaving only the wires and junction in the hotter parts.

3. Boiling Points

Boiling points play an important part in the definition of the International Temperature Scale, since 3 of the 4 points upon which the scale between −190 and 600 °C is based, are the boiling points of oxygen, water, and sulfur. However, boiling points with the exception of that of water, are seldom used in the calibration of thermocouples and consequently the methods of realizing these various points will be mentioned only briefly here. References are given to complete discussions for those interested, as boiling points might profitably be employed to a greater extent, when a platinum-resistance thermometer or a stirred liquid bath is not available.

(a) Steam Point. The temperature of condensing water vapor is realized experimentally by the use of a hypsometer so constructed as to avoid superheat of the vapor around the thermocouple and contamination with air and other impurities. Simple types of hypsometers are shown in various trade catalogs. Mueller and Sligh [7] give a detailed description of a hypsometer used in precision measurements. If the proper conditions are attained, the observed emf of the couple will be independent of the rate of heat supply to the boiler, the length of time the hypsometer has been in operation, and the depth of immersion of the couple. The couple for some distance from the junction must be shielded from radiation from hotter and colder surfaces. The relation between the temperature (t_p) in °C and the pressure (p) for the range 680 to 780 mm of Hg is given by

$$t_p = 100.000 + 0.0367(p - 760) - 0.000023(p - 760)^2$$

The steam point as realized by utilizing the condensing vapor in a hypsometer is certainly accurate 0.01 °C. An accuracy of about 1 °C can be obtained by merely immersing a couple in boiling water.

(b) Sulfur, Benzophenone, and Naphthalene Points. These points are near the freezing points of available pure metals and are very seldom used in the calibration of thermocouples. The specifications to be followed in realizing the sulfur point are given in the International Temperature Scale.[8] Detailed description of the apparatus and precautions to be observed for the sulfur boiling point are given by Mueller and Burgess.[9] The procedure and apparatus for realizing the boiling points of naphthalene and benzophenone are the same as those for the boiling point of sulfur. Detailed information regarding these points is given by Waidner and Burgess [10] and by Finck and Wilhelm.[11]

(c) Oxygen Point.* The temperature of equilibrium between liquid and gaseous oxygen is best realized experimentally by the static method, the oxygen vapor-pressure thermometer being compared with the thermocouple to be calibrated in a suitable low-temperature bath. An oxygen vapor-pressure thermometer is nothing more than a glass tube containing very pure oxygen at a pressure of several atmospheres at room temperature, and connected to a mercury-filled manometer for measuring the pressure in the tube. When the thermometer tube is immersed in the bath, part of the oxygen liquifies. The temperature (t_p) in °C of the bath is related to the pressure (p) in the thermometer by $t_p = -182.97 + 0.0126 (p-760) - 0.0000065 (p-760)^2$ in the range 680 to 780 mm of Hg. This requires that the temperature of the bath be kept within the limits −183.9 to −182.7 °C. This is most conveniently done by stirring liquid oxygen in a dewar flask.

(d) Carbon-dioxide Point.* Although the sublimation point of carbon dioxide is not a boiling point, the highest accuracy is obtained in utilizing this point, by employing the same method as that for the boiling point of oxygen. An instrument of this type suitable for use as a carbon-dioxide vapor-pressure thermometer is container type 3, described by Meyers and Van Dusen.[12] The sublimation point of carbon dioxide may also be utilized by immersing the couple in a slush made by mixing carbon-dioxide snow with a liquid such as acetone. The slush should be stirred and the air excluded from the vapor above the surface of the slush. Whereas the accuracy obtained with a vapor-pressure thermometer is of the order of a few hundredths of a degree, an accuracy of 1 °C is all that can be claimed for the temperature of the slush.

IV. Calibration by Comparison Methods

The calibration of a thermocouple by comparison with a working standard is sufficiently accurate for most purposes and can be done conveniently in most industrial and technical laboratories. The success of this method usually depends upon the ability of the observer to bring the junction of the couple to the same temperature as the actuating element of the standard, such as the hot junction of a standard thermocouple or the bulb of a resistance or liquid-in-glass thermometer. The accuracy obtained is further limited by the accuracy of the standard. Of course, the reference-junction temperature must be known, but this can usually be controlled by using an ice bath as described earlier or measured by a liquid-in-glass thermometer. The method of bringing the junction of the couple to the same temperature as that of the actuating element of the standard depends upon the type of couple, type of standard, and the method of heating.

* The use of this point is more fully discussed by R. B. Scott elsewhere in this Symposium.

1. Platinum-Rhodium Thermocouples

Platinum-rhodium thermocouples, either the 10- or 13-per cent rhodium, are seldom used for accurate measurements below 300 °C (572 °F) and are practically never used below 0 °C, because the thermal emf per degree of these couples decreases rapidly at low temperatures, becoming zero at about −138 °C (−216 °F). These couples are usually calibrated above 300 °C by comparison with standard thermocouples in electrically heated furnaces. The standard couple may be either a 10- or 13-per cent rhodium couple that has been calibrated at fixed points or by comparison with other couples so calibrated.

The method employed at the National Bureau of Standards for the comparison of two such couples permits simultaneous reading of the emf of each couple without waiting for the furnace to come to a constant temperature. In order to insure equality of temperature between the measuring junctions of the couples, they are welded together. A separate potentiometer is used to measure each emf, one connected to each thermocouple, and each potentiometer is provided with a reflecting galvanometer. The two spots of light are reflected onto a single scale, the galvanometers being set in such a position that the spots coincide at the zero point on the scale when the circuits are open and therefore also when the potentiometers are set to balance the emf of each thermocouple. Simultaneous readings are obtained by setting one potentiometer to a desired value and adjusting the other so that both spots of light pass across the zero of the scale together as the temperature of the furnace is raised or lowered.

By making observations first with a rising and then with a falling temperature, the rates of rise and fall being approximately equal, and taking the means of the results found, several minor errors such as those due to differences in the periods of the galvanomters, etc., are eliminated or greatly reduced. The differences between the values observed with rising and falling temperatures are usually less than 5 μv with platinum-rhodium couples, if the periods of the galvanometers are approximately the same.

This method is particularly adapted to the calibration of couples at any number of selected points. For example, if it is desired to determine the temperature of a couple corresponding to 10.0 mv, this emf is set up on the potentiometer connected to this couple, the emf of the standard couple observed as described above, and the temperature obtained from the emf of the standard. If it is desired to determine the emf of a couple corresponding to 1000 °C, the emf of the standard corresponding to this temperature is set up on the potentiometer connected to the standard and the emf of the couple being tested is observed directly.

In order to calibrate a couple in the least possible time by this method, it is necessary to use a furnace that is so contructed that it will cool rapidly. The heating element of the furnace used at the National Bureau of Standards for the routine testing of couples consists of a nickel(80)-chromium(20) tube clamped between two water-cooled terminals. The tube, which is $\frac{13}{16}$ inch inside diameter, $1\frac{5}{16}$ inches outside diameter, and 24 inches long, is heated electrically, the tube itself serving as the heating element or resistor. The large current necessary to heat the tube is obtained from a transformer. A large cylindrical shield of sheet metal is mounted around the heating tube to reduce the radiation loss. To minimize lag no thermal insulation is used between the heating tube and the radiation shield. The middle part of this furnace for about 18 inches is at practically a uniform temperature and the water-cooled terminals produce a very sharp temperature gradient at each end. This furnace can be heated to 1200 °C in about 5 minutes with 12 kw and, if all the power is shut off, will cool from this temperature to 300 °C in about the same time. This type of furnace can be used up to 1250 °C (2282 °F).

The thermocouples are insulated and protected by porcelain tubes. It is essential that the two potentiometer and thermocouple circuits be separate except at the point where the junctions are welded together. The cold junctions are maintained at 0 °C.

The above method and apparatus were devised primarily for the rapid testing of couples, but it is not necessary to follow this method literally or to procure identical apparatus to obtain good results. If it is not convenient to weld the junctions of the couples together, they may be brought into fairly good contact by wrapping with platinum wire or foil. The only advantage of the furnace described above, over any other type of furnace in which several inches of the couples may be heated to a uniform temperature, is the flexibility of control. Electric tube furnaces suitable for such comparison tests can be obtained, designed to operate on either 110 or 220 v, and may be obtained equipped with an adjustable rheostat for regulating the current. For temperatures up to 1150 °C (2102 °F), a furnace with a heating element of nickel(80)-chromium(20) will suffice. Furnaces with heating elements of platinum or platinum-rhodium are available for higher temperatures. A convenient size of heating tube is 1 inch in diameter and 18 inches long. Even though the furnace tube is kept fairly clean, it is advisable to protect platinum-rhodium couples by a porcelain tube. If two potentiometers are not available for taking simultaneous readings, the furnace may be brought to essentially a constant temperature and the emf of each couple read alternately on one instrument.

When the couples are calibrated by welding or wrapping the junctions together, the difference between the temperatures of the junctions should not be great even when the temperature of the furnace is changing. If it is necessary or advisable to calibrate the couples without removing them from the protection tubes, then the junction of the couple being tested and that of the standard should be brought as close together as possible in a uniformly heated portion of the furnace. In this case it is necessary that the furnace be brought to approximately a constant temperature before taking observations. It is usually not possible to maintain the reference junctions at 0 °C when the couples are completely enclosed in protection tubes. However, extension leads may be used with the couple or the temperature of the reference junctions may be measured with a thermometer.

There are a number of other methods of heating and of bringing the junctions to approximately the same temperature, for example, inserting the couples properly protected into a bath of molten metal or into holes drilled in a large metal block. The block of metal may be heated in a muffle furnace or, if made of a good thermal conductor such as copper, may be heated electrically. Tin, which has a low melting point, 232 °C (450 °F), and low volatility, makes a satisfactory bath material. The couples should be immersed to the same depth with the junctions close together. Porcelain tubes are sufficient protection, but to avoid breakage by thermal shock when immersed in molten metal it is preferable to place them inside of secondary tubes of iron, nickel-chromium, graphite, or similar material. In all of these methods, particularly in those cases in which the junctions of the couples are not brought into direct contact, it is important that the depth of immersion be sufficient to eliminate cooling or heating of the junctions by heat flow along the thermocouple and the insulating and protecting tubes. This can be determined by observing the change in the emf of the couple as the depth of immersion is changed slightly. If proper precautions are taken the accuracy yielded by any method of heating or bringing the junctions to the same temperature may be as great as that obtained by any other method.

2. Base-metal Thermocouples in Laboratory Furnaces

The methods of testing base-metal thermocouples above room temperature are generally the same as those just described for testing rare-metal couples with the exception, in some cases, of the methods of bringing the junctions of the standard and the couple being tested to the same temperature and the methods of protecting platinum-rhodium standards from contamination. One arrangement of bringing the junction of a platinum-rhodium standard to the same temperature as that of a large base-metal couple for accurate calibration is to insert the junction of the standard into a small hole (about 1.5 mm in diameter) drilled in the hot junction of the base-metal couple as shown in Fig. 3. The platinum-rhodium standard is protected by porcelain tubes to within a few millimeters of the hot junction, and the end of the porcelain tube is sealed to the couple by Pyrex glass or by a small amount of kaolin and water-glass cement. This prevents contamination of the standard couple, with the exception of the small length of 2 or 3 mm, which is necessarily in contact with the base-metal couple. If the furnace is uniformly heated in this region (and it is of little value to make such a test unless it is) contamination at this point will not cause any error. If the wire becomes brittle at the junction this part of the wire may be cut off and enough wire drawn through the seal to form a new junction. The seal should be examined after each test and remade if it does not appear to be good. More than one base-metal couple may be welded together and the hole drilled in the composite junction. The couples should be clamped in place so that the junctions remain in contact. If two potentiometers are used for taking simultaneous readings, the temperature of the furnace may be changing as much as a few degrees per minute during an observation, but if a single instrument is used for measuring the emf, the furnace temperature should be maintained practically constant during observations.

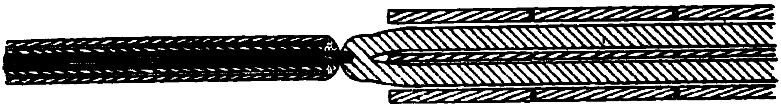

FIG. 3. Arrangement to assure good thermal contact between the junction of a base-metal couple and that of a protected platinum-rhodium couple.

In testing one or more small base-metal couples, they may be welded to the junction of the standard. If a base-metal standard is used, the best method is to weld all the junctions together. If a large number of base-metal couples are to be tested at the same temperature, the method of immersing the couples in a molten-metal bath or into holes drilled in a large copper block is very advantageous. If a tin bath is used, iron or nickel-chromium tubes are sufficient protection for base-metal couples. When wires, insulators, and protection tubes of base-metal couples are large, tests should be made to insure that the depth of immersion is sufficient to eliminate heating or cooling of the junction by heat flow along these materials.

3. Thermocouples in Fixed Installations

After thermocouples have been used for some time at high temperatures, it is difficult if not impossible to determine how much the calibrations are in error by removing them from an installation and testing in a laboratory furnace. The thermocouples are usually inhomogeneous after such use and in such a condition the emf developed by the couples depends upon the temperature distribution along the wires. If possible such couples should be tested under the same conditions and in the same installation in which they are used. Although it is not usually possible to obtain as high a precision by testing the couples in place as is obtained in laboratory tests, the results are far more accurate in the sense of being representative of the behavior of the couples.

The exact method of procedure depends upon the type of installation. A standard couple is usually employed with extension leads and a portable high-resistance millivoltmeter or preferably a portable potentiometer. In this case, as in the calibration of any couple by comparison methods, the main objective is to bring the hot junction to the same temperature as that of the couple being tested. One method is to drill a hole in the furnace at the side of each couple permanently installed, large enough to permit insertion of the checking couples. The hole is kept plugged, except when tests are being made. The standard couple is immersed in the furnace through this hole to the same depth as the couple being tested, with the hot junction ends of the protection tubes as close together as possible.

In many installations the base-metal couple and protecting tube are mounted inside another protecting tube of iron, fire clay, carborundum, or some other refractory which is permanently cemented or fastened into the furnace wall. Frequently there is room to insert a small test couple in this outer tube alongside of the fixed couple. A third method, much less satisfactory, is to wait until the furnace has reached a constant temperature and make observations with the couple being tested, then remove this couple from the furnace, and insert the standard couple to the same depth.

If desired, comparisons can be made preferably by either of the first or second methods at several temperatures, and a curve obtained for each permanently installed couple showing the necessary corrections to be applied to its readings. Although testing a thermocouple at one temperature yields some information, it is not safe to assume that the changes in the emf of the couple are proportional to the temperature or to the emf. For example, it has been observed that a couple which had changed in use by the equivalent of 9 °C at 315 °C had changed only the equivalent of 6 °C at 1100 °C.

It may be thought that this method of checking couples is unsatisfactory because, in most furnaces used in industrial processes, large temperature gradients exist and there is no certainty that the standard couple is at the same temperature as the couple being tested. This objection, however, is not serious, because if temperature gradients do exist of such a magnitude as to cause much difference in temperature between two similarly mounted thermocouples located close together, the reading of the standard couple represents the temperature of the fixed couple as closely as the temperature of the latter represents that of the furnace.

The principal advantage of this method is that the thermocouple, leads, and indicator are tested as a unit and under the conditions of use.

4. Thermocouples in Stirred Liquid Baths

Thermocouples and resistance thermometers are not usually directly compared above 300 °C because of the difficulty encountered in bringing the thermocouple junction and the thermometer bulb to the same temperature, but these two types of instruments may be very accurately compared below 300 °C where a stirred liquid bath can be conveniently used. A type of bath suitable for use above 0 °C is shown in figure 5 of a paper by N. S. Osborne.[13] The container, which is insulated on the outside, consists of two cylindrical vertical tubes connected at the bottom and near the top by rectangular ports. A frame carrying the heating element, cooling coils if desired, and stirring propeller are inserted in one of the vertical tubes. The instruments being compared are placed in the other vertical tube and held in place by any convenient means. The chief advantage of this arrangement is that local irregularities due to direct conduction from the vicinity of the heating or cooling elements are eliminated. A stirred liquid bath for use below 0 °C has been described by Scott and Brickwedde.[14]

The liquids used in the baths should be capable of being stirred readily at any temperature at which they are used and they should not be highly flammable. At the National Bureau of Standards, oil is used between 100 and 300 °C, water in the range 0 to 100 °C, mixtures of carbon tetrachloride and chloroform in the range 0 to −75 °C, a five-component mixture containing 14.5 per cent of chloroform, 25.3 per cent of methylene chloride, 33.4 per cent of ethyl bromide, 10.4 per cent of *trans*-dichloroethylene, and 16.4 per cent of trichloroethylene in the range −75 to −140 °C, and commercial propane below −140 °C. Propane is highly flammable, and every precaution must be taken to prevent it from mixing with liquid air or oxygen. A complete series of nonflammable liquids for cryostats is given by C. W. Kanolt [15] for temperatures down to −150 °C.

A number of couples can be calibrated at one time in a stirred liquid bath. Platinum-resistance or liquid-in-glass thermometers or thermocouples may be used as standards.

V. Methods of Interpolating Between Calibration Points

1. Platinum-Rhodium Couples

After a thermocouple has been calibrated at a number of points, the next requirement is a convenient means of obtaining corresponding values of emf and temperature at other points. A curve may be drawn or a table giving corresponding temperature and emf values may be prepared. The values in such a table may be obtained by computing an empirical equation or series of equations through the calibration points, by direct interpolation between points, or by drawing a difference curve from an arbitrary reference table which closely approximates the temperature-emf relation of the couple. The method to be selected for a particular calibration depends upon such factors as the type of couple, number of calibration points, temperature range, accuracy required, and personal preference.

For the highest accuracy in the range 660 to 1063 °C with platinum to platinum-10 per cent rhodium thermocouples, the method is that prescribed in the International Temperature Scale. An equation of the form $e=a+bt+ct^2$, where a, b, and c are constants determined by calibration at the freezing points of gold, silver, and antimony, is used. By calibrating the couple also at the freezing point of zinc and using an equation of the form $e=a'+b't+c't^2+d't^3$, the temperature range can be extended down to 400 °C without introducing an uncertainty [16] of more than 0.1 °C in the range 660 to 1063 °C. By calibrating the couple at the freezing points of gold, antimony, and zinc and using an equation of the form $e=a''+b''t+c''t^2$, a calibration is obtained for the range 400 to 1100 °C, which agrees (reference 16) with the International Temperature Scale to 0.5 °C. The freezing point of copper may be used instead of the gold point, and the aluminum point used instead of the antimony point without introducing an additional uncertainty (reference 16) of more than 0.1 °C.

For temperatures outside the range 660 to 1063 °C, the method of drawing a smooth curve through the temperature and emf values has just as much claim to accuracy as the method of passing empirical equations through the calibration points, because an empirical equation performs the same function as a curved ruler. For the temperature range 0 to 1500 °C, a curve for interpolation to 1 or 2 °C requires calibration points not more than 200 °C apart and a careful plot on a large sheet of paper, which is tedious to read. A reduction in the number of calibration points increases the uncertainty proportionately. If, however, we plot as ordinates the differences between the observed emf and that calculated from the first degree equation $e = 10t$, and emf as abscissas, the difference at intermediate points may be taken from the curve and added to the quantity $10t$ to obtain values of emf corresponding to the appropriate temperature in which the uncertainty in the interpolated values is much less than in the case in which the emf is plotted directly against the temperature. If we go one step further and plot differences from an arbitrary reference table the values of which closely represent the form the temperature-emf relation for the type of couple in question, the maximum differences to be plotted will be only a few degrees. In this way interpolated values are obtained in which the uncertainty in the interpolated values is not appreciably greater than that at the calibration points. The more accurately the values in the arbitrary reference table conform to the emf-temperature relation of actual couples, the fewer the number of calibration points required for a given accuracy.

Reference tables [17] for platinum-rhodium thermocouples which are based on the temperature-emf relations of a considerable number of representative couples from various sources have recently been published. These tables represent accurately the shape of the relations for both the 10 and 13 per cent rhodium couples in the entire range 0 to 1700 °C. The difference curve for any couple from the appropriate table is practically a straight line.

In the calibration of platinum to platinum-10 per cent rhodium thermocouples to be used as working standards at the National Bureau of Standards, the emf is observed at the freezing points of gold, silver, antimony, zinc, lead, and tin and at the boiling point of water. The constants in the equation $e = a + bt + ct^2$ are computed from the observations at the gold, silver, and antimony points. Values in the range 660 to 1063 °C, computed from this equation, and the four observed values below 660 °C are used to construct a difference curve from the reference table mentioned previously. This difference curve is then extended graphically above 1063 °C. Values taken from this difference curve when added algebraically to the values in the reference table yield the corresponding temperature-emf values at any temperature. A numerical example follows.

Table 4. Data for Construction of Difference Curve.

Temperature, t °C	Observed emf thermocouple H4 e µv	Emf values from table 2, Research Paper 530 e_t µv	Difference $\Delta e = e_t - e$ µv	Temperature, t °C	Observed emf thermocouple H4 e µv	Emf values from table 2, Research Paper 530 e_t µv	Difference $\Delta e = e_t - e$ µv
0.0	0.0	0.0	0.0	700.0	6269.9	6260.0	−9.9
100.0	644.0	643.0	−1.0	800.0	7342.4	7330.0	−12.4
231.9	1712.0	1709.0	−3.0	900.0	8447.0	8433.3	−13.7
327.35	2570.7	2566.6	−4.1	960.5	9131.0	9117.0	−14.0
419.48	3441.8	3436.3	−5.5	1000.0	9583.9	9569.0	−14.9
630.5	5543.5	5535.0	−8.5	1063.0	10316.7	10301.0	−15.7

The observed values of emf at the calibration points are given in Table 4 together with the values at 100 °C intervals from 660 to 1063 °C computed from the equation

$$e = -335.4 + 8.3087\,t + 0.0016106\,t^2$$

Corresponding values of e and Δe are plotted in Fig. 4.

For accurate extrapolation above the gold point it is essential that the shape of the emf-temperature relation given in the reference table conform closely to that of actual thermocouples so that the difference curves will be linear both above and below this point. If the difference curve has a large curvature or if there is an abrupt change in slope above the gold point, the extrapolation of the difference curve may involve considerable uncertainty. The difference curves of actual thermocouples both 10- and 13-per cent rhodium alloys from the reference tables given in Research Paper 530 are in most cases linear in the entire range 0 to 1700 °C and the difference curves can therefore be extrapolated with but little uncertainty. The extrapolated values for a number of thermocouples have been checked by means of actual comparison with an optical pyrometer, and in no case was the difference as great as 3 °C at 1500 °C and in most cases it was not over 1 °C. These differences are not much greater than the accidental errors in the comparisons.

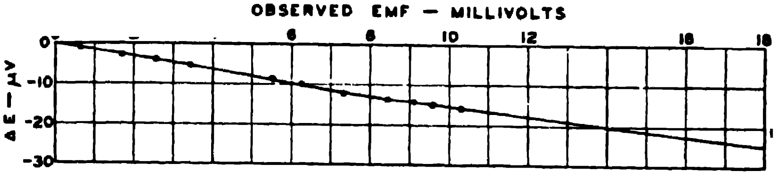

Fig. 4. Difference curve for a platinum 10 per cent rhodium couple from reference table in Bureau of Standards Research Paper 530.

Difference curves can be drawn from observations obtained in comparison calibrations as well as for observations at fixed points. Two points (accurate to ± 1 °C at about 600 and 1200 °C) are usually sufficient to determine the difference curve from the tables in Research Paper 530 for either a 10- or a 13-per cent rhodium couple, such that the resulting calibration is accurate to ±2 °C at any point in the range 0 to 1200 °C and to ±3 °C up to 1500 °C.

2. Copper-Constantan Couples

The relation between the temperature and emf of copper-constantan thermocouples [18] has been very well established in the range −200 to +300 °C. The temperature of the measuring junction of such a couple can be very accurately determined in this range with a platinum-resistance thermometer in a stirred liquid bath. Consequently the accuracy obtained with this type of couple is, in general, limited by the stability of the constantan wire above 200 °C and by the accuracy of the emf measurements or the homogeneity of the wire below 100 °C. The stability of the larger sizes of wire is greater than that of the smaller wires under the same conditions.

Fig. 5 shows a difference curve from Adams' table [19] for a typical copper-constantan thermocouple. Two points above and two below 0 °C suitably spaced are usually sufficient to give an accuracy of 0.3 °C.

Equations are used to good advantage with copper-constantan couples for interpolating between calibration points, but it has not been demonstrated that the accuracy obtained with equations is any greater than that obtained by drawing difference curves from Adams' table except when the differences are large. One convenient method of obtaining a calibration accurate to ±0.2 °C in the range 0 to 100 °C is to use an equation of the form $e = at + 0.04t^2$ where a is a constant determined by calibration at 100 °C, e the emf in microvolts and t the temperature in °C. An equation of the form $e = at + bt^2 + ct^3$ where a, b, and c are constants determined by calibration at three points (about 100, 200, and 300 °C), will give interpolated values as accurately as the couple can be relied upon to retain its calibration (about 0.2 °C). The same type of equation with the constants determined at three points about equally spaced in the range 0 to −190 °C, may be used in this range to give interpolated values almost as accurately as the emf can ordinarily be measured (about 2 μv). An equation of the form $e = at + bt^2$ will yield interpolated values in the range 0 to 100 °C almost as accurately as the emf is determined at the calibration points, if the constants are determined by calibration at about 50 and 100 °C. The same is true of this equation in the range 0 to −100 °C if the constants are determined at −50 and −100 °C.

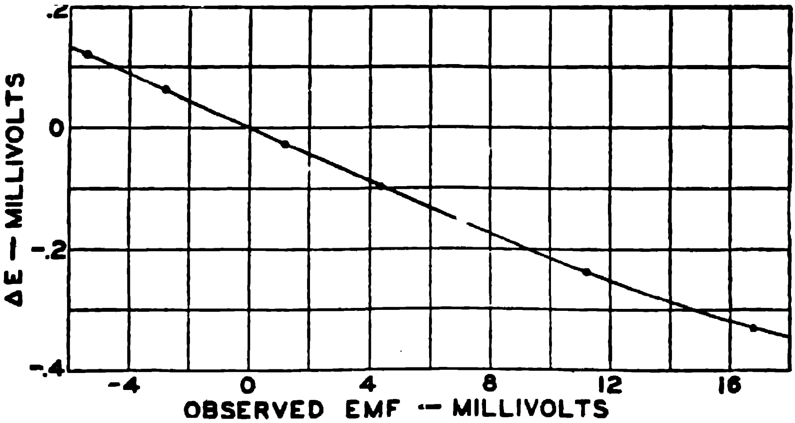

FIG. 5. Difference curve for a copper-constantan couple from Adams' table in "International Critical Tables."

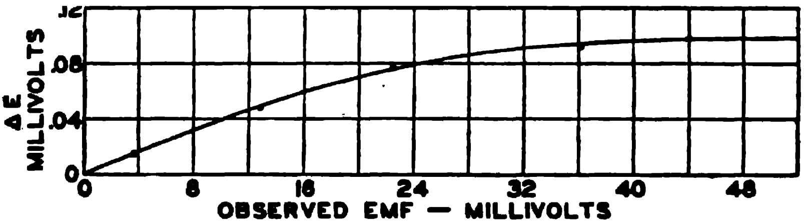

FIG. 6. Difference curve for a Chromel-Alumel couple from table in Bureau of Standards Research Paper 767.

3. Chromel-Alumel Couples

Fig. 6 shows a difference curve for a typical chromel-alumel thermocouple from the NBS standard tables[20] given on page 1301 of the appendix of this book. The difference curve from these tables can be determined in the range 0 to 1300 °C (2372 °F) with an uncertainty not more than 1 °C greater than at the calibration points by calibration at 500, 800, and 1100 °C (or at 1000, 1600, and 2000 °F).

These tables represent the average temperature-emf relation of chromel-alumel couples now being manufactured.

Little success has been met in fitting equations to the calibration of chromel-alumel thermocouples in the range 0 to 300 °C. An equation of the form $e = at + bt^2 + ct^3$ will be in error by 1 °C at 50 °C if the constants are determined by calibration at about 100, 200, and 300 °C. However, it will be accurate to about 0.5 °C at 150 °C and to about 0.2 °C between 200 and 300 °C. In the range 0 to −190 °C, an equation through three points about equally spaced will give interpolated values in which the uncertainty is not more than 2 μv greater than at the calibration points.

4. Iron-Constantan Couples

The various reference tables for iron-constantan thermocouples are discussed in a recently published paper.[18] Fig. 7 shows the differences between the calibrations of several iron-constantan thermocouples and the reference table determined at the National Bureau of Standards. This table differs by about 4 °C at 200 °C and by about 2 °C at 650 °C from the table which has been widely used by instrument companies and which is given in skeleton form in Bureau of Standards Technologic Paper T170, p. 306, and the "International Critical Tables," Vol. 1, p. 59.

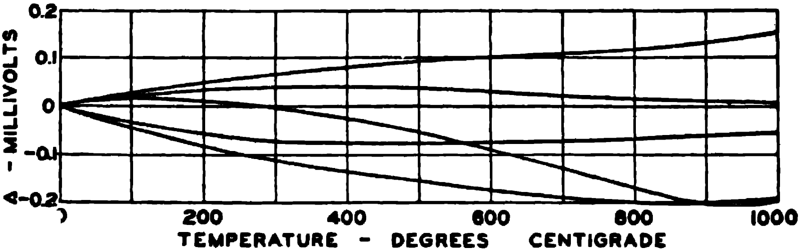

FIG. 7. Differences between the calibrations of some iron-constantan thermocouples and the Table in National Bureau of Standards RP 1080.

We have no data as to how closely the temperature-emf relations of iron-constantan couples may be fitted by equations.

VI. Reference-junction Corrections

It is not always possible to maintain the reference junctions (commonly called cold junctions) at a desired temperature during the calibration of a thermocouple, but if the temperature of the reference junctions is measured it is possible to apply corrections to the observed emf which will yield a calibration with the desired reference-junction temperature. If the emf of the couple is measured with the reference junctions at temperature t, and a calibration is desired with these junctions at temperature t_0, the measured emf may be corrected for a reference-junction temperature of t_0 by adding to the observed value the emf which the couple would give if the reference junctions were at t_0 and the measuring junction at t. For example, suppose the observed emf of a platinum-10 per cent rhodium thermocouple with the measuring junction at 1000 °C and the reference junction at 25 °C is 9.43 mv, and the emf of the couple with the measuring junction at 1000 °C and the reference junctions at 0 °C is required. The emf of the couple when the reference junctions are at 0 °C and the measuring junction at 25 °C is 0.14 mv, then the sum of these emf (9.43 and 0.14) gives the desired value.

The sign of the corrections must be considered when applying these corrections. For example, suppose the observed emf of the couple with the measuring junction at 1000 °C and the reference junctions at 0 °C is 9.57 mv and the emf of the couple with the measuring junction at 1000 °C and the cold junctions at 25 °C is required. The emf of the couple when the reference junction is at 25 °C and the measuring junction at 0 °C is −0.14 mv, and when this is added to the observed emf the desired value 9.43 mv is obtained. Whether the reference-junction correction is positive or negative should not cause any confusion if it is remembered that the emf of the couple is lowered by bringing the junction temperatures closer together and increased by making the difference greater.

In the calibration of couples the temperature-emf relation is not always accurately determined in the range of reference-junction temperatures, in which case the average temperature-emf relation of the type of couple may be used. The average relations for the various types of couples are given in Table 5. The errors caused by using these average relations instead of the actual relation for a particular couple are, in general, less than 1 °C.

Table 5. Average Temperature-Emf Relations for Thermocouples for Applying Reference-Junction Corrections.

Temperature		Electromotive force			
(°C)	(°F)	Platinum-rhodium [1] (mv)	Chromel-alumel (mv)	Iron-constantan (mv)	Copper-constantan (mv)
−20	−4	−0.101	−0.77	−1.03	−0.75
−15	5	−.077	−.58	−.78	−.57
−10	14	−.052	−.39	−.52	−.38
−5	23	−.026	−.20	−.26	−.19
0	32	.000	.00	.00	.00
5	41	.027	.20	.26	.19
10	50	.054	.40	.52	.39
15	59	.082	.60	.78	.59
20	68	.111	.80	1.05	.79
25	77	.141	1.00	1.31	.99
30	86	.171	1.20	1.58	1.19
35	95	.201	1.40	1.85	1.40
40	104	.232	1.61	2.12	1.61
45	113	.264	1.81	2.39	1.82
50	122	.297	2.02	2.66	2.03

[1] The values in this column apply for either the 10- or 13-per cent rhodium couple. The difference between the average temperature-emf relations in this range does not exceed 5 μv.

If the thermocouple is very short, so that the reference junctions are near the furnace and subject to considerable variations or uncertainty in temperature, it is usually more convenient to use extension leads to transfer the reference junctions to a region of more constant temperature than to measure the temperature of the reference junctions near the furnace. The extension leads of base-metal couples are usually made of the same materials as the thermocouple wires, but in the case of platinum-rhodium couples a copper lead is connected to the platinum-rhodium wire and a copper-nickel lead to the platinum wire. Leads for any of the couples discussed here are available at all the pyrometer instrument manufacturers. Although the temperature-emf relation of the copper, copper-nickel lead wire is practically the same as that of platinum-rhodium couples, the individual lead wires are not identical thermoelectrically with the couple wires to which they are attached and.

therefore, the two junctions where the leads are attached to the couple should be kept at nearly the same temperature. This is not necessary in the case of base-metal couples when each lead and couple wire to which it is attached are the same material.

VII. Testing of Thermocouple Materials

Thermocouples are ordinarily made up to yield a specified emf at one or more temperatures, and in order to select and match materials to do this a convenient method of testing each element is required. One method of accomplishing this is to determine the thermal emf of the various materials against some stable and reproducible material. At low temperatures copper is sometimes used for this purpose, but platinum appears to be the most satisfactory because it can be used at any temperature up to its melting point, can be freed from all traces of impurities, and can be readily annealed in air. Two samples of platinum, both of which are spectrochemically pure, may differ slightly in thermal emf, but the same is true of any other metal. To avoid the ambiguity that might arise from this fact, the thermal emf of thermocouple materials tested at the National Bureau of Standards (since 1922) is referred to an arbitrary piece of platinum designated as standard Pt 27. This standard is spectrochemically pure, has been thoroughly annealed, and although it may not be the purest platinum that has been prepared, serves as a satisfactory standard to which the thermal emf of other materials may be referred. However, there is nothing to prevent any other laboratory from setting up a laboratory standard for their own use, but in order that the various laboratories and manufacturers may specify and express values of thermal emf on a common basis, a common and ultimate standard is necessary.

Platinum is used as a working standard for testing thermocouple materials in some laboratories, but it is generally more convenient to use a working standard of the same material as that being tested. In any case the thermal emf of a material against the standard Pt 27 is the algebraic sum of the emf of the material against the working standard and the emf of the working standard against the standard Pt 27 (the law of intermediate metals). When platinum is used as a working standard in testing some other material, the thermal emf measured is large. To obtain the thermal emf of the material against the standard Pt 27, the relatively small emf of the platinum working standard against the standard Pt 27 is added to the large measured emf. When the working standard is of the same kind of material as that being tested, the thermal emf measured is small. To obtain the thermal emf of the material against the standard Pt 27 in this case, the relatively large emf of the working standard against the standard Pt 27 is added to the small measured emf.

Except in the case of constantan, two samples of a similar material which will develop more than 0.5 μv/°C against one another are exceptional. In most cases the value is less than 0.2 μv/°C. Even in the case of constantan, the thermal emf between 2 extreme samples does not exceed 3 μv/°C. Therefore, in determining the difference in thermal emf between two samples of a similar material, it is not necessary to measure the temperature accurately.

The average thermal emf/°C of platinum against other thermocouple materials is given in Table 6. It is seen that in measuring the thermal emf of these materials directly against platinum working standards, it is necessary to measure an emf which changes by a large amount for a small change in temperature. An accurate measurement of the emf corresponding to a given temperature, therefore, requires an accurate measurement of the temperature of the junctions. The neces-

Table 6. Average Thermal[1] Emf/°C of Platinum against other Thermocouple Materials.

Material	Temperature (°C)	Average change in thermal emf with temperature (μv/°C)
Platinum-10 per cent rhodium	1000	11.5
Platinum-13 per cent rhodium	1000	13.0
Chromel	870	31.7
Alumel	870	8.7
Iron	600	11.4
Constantan	600	47.0
Constantan	100	37.0
Copper	100	9.25

[1] Complete tables giving the average thermal emf of platinum-10 per cent rhodium, and platinum-13 per cent rhodium against platinum are given in Research Paper 530. The average thermal emf of chromel and of alumel against platinum are given in Research Paper 767 and of iron, copper, and constantan against platinum in Research Paper RP1080.

sity for this accurate measurement of temperature, however, is avoided when the measurements are made by using a working standard of material similar to that being tested, since in this case the emf developed is small and changes very little even for large changes in temperature. In the latter method, the accurate measurement of temperature is not entirely avoided but merely shifted to the laboratory that determines the thermal emf of the working standards against the standard Pt *27*.

The small thermal emf of a platinum working standard against the standard Pt *27* at any temperature can be determined as accurately as the emf can be measured. These standards are subject to change during use but, if properly used and occasionally checked, can be relied upon to about 10 μv at 1000 °C. The thermal emf of working standards of other materials is determined and certified at the National Bureau of Standards to the equivalent of ± 1 °C at high temperatures.

In any event the testing of a thermocouple material is essentially the determination of the emf of a thermocouple in which the material being tested is one element and a working standard the other. Some of the precautions that must be observed to obtain accurate results are given in the following sections.

1. Platinum

The thermal emf of thermocouple platinum against the standard Pt *27* is usually less than 100 μv at 1200 °C and in testing one sample of platinum against another it is not necessary to measure the temperature of the hot junction to closer than 25 °C to obtain a comparison accurate to 2 μv. The reference-junction temperature need not be accurately controlled. The platinum standard (*i.e.*, the wire previously compared with the standard Pt *27*) is welded to the wire being tested to form a couple and the emf measured at one or more temperatures by any of the methods described for calibrating platinum-rhodium thermocouples. The wires should be carefully insulated and protected. Measurements at two temperatures, about 600 and 1200 °C, are sufficient to give the emf at any temperature as the emf is small and practically proportional to the temperature.

In many laboratories the platinum standard and the platinum element of the couple used to measure the temperature are one and the same. The sample or wire being tested is then welded to the junction of the couple and the emf of the couple and that between the two platinum wires are measured simultaneously with two potentiometers or alternately with one instrument. Simultaneous readings of these electromotive forces should not be made with a millivoltmeter or with a current flowing in either circuit because one wire is common to both circuits and in this case the potential difference measured by one instrument is influenced by the current flowing in the other circuit. However, this objection is not encountered in the method described above in which the platinum standard is not the same wire as the platinum of the thermocouple.

2. Platinum-Rhodium

The testing of platinum-rhodium thermocouple wire directly against platinum is exactly the same as the calibration of platinum-rhodium thermocouples. Platinum against platinum-10 per cent rhodium gives 11.5 μv/°C and platinum against platinum-13 per cent rhodium gives about 13 μv/°C at 1000 °C. Therefore, in order to determine the thermal emf of a sample of platinum-rhodium against platinum to ± 20 μv, it is necessary to measure the temperature to ± 1.5° C. Such an accuracy in temperature measurements is obtained only with a very homogeneous and accurately calibrated couple in a uniformly heated furnace, but if the emf of one sample of wire is known with this accuracy, it may be used to determine the emf of other samples without the necessity of accurately measuring the temperature. For example, the thermal emf per degree of any sample of platinum-10 per cent rhodium against any other sample rarely exceeds 0.2 μv/°C (200 μv at 1000 °C). Therefore, if the thermal emf of one sample against platinum is known to ± 20 μv at 1000 °C, the emf of other samples against the same platinum can be determined to about the same accuracy by comparing the samples of platinum-rhodium and measuring the temperature of the hot junction to 10 or 20 °C. The same applies for platinum-13 per cent rhodium.

The working standard used to determine the thermal emf of the platinum-rhodium may be a sample of platinum, of platinum-rhodium, or either element of the thermocouple used in measuring the temperature. Platinum-10 per cent rhodium against platinum-13 per cent rhodium gives about 1.5 μv/°C at 1000 °C so that if the thermal emf of one of these materials against platinum is known to ± 20 μv at 1000 °C, the thermal emf of the other against the same platinum can be determined to ± 30 μv by comparing the two and measuring the temperature to ± 6°C.

A number of wires can be welded together and tested by any of these methods.

3. Base-metal Thermocouple Materials

(a) At High Temperatures. In testing base-metal thermocouple materials (alumel, chromel, constantan, copper, and iron) the procedure is very much the same as in calibrating base-metal thermocouples. Although such thermal-emf measurements are ultimately referred to platinum, it is not necessary to measure each sample directly against platinum. When the measurements are made against platinum (and this must frequently be done), the platinum wire should be sealed through the end of a glazed porcelain protection tube with pyrex glass, leaving about 1 cm of the wire exposed for welding to the base-metal wire or wires. The largest uncertainty in the measurements arises from the uncertainty in the determination of the temperature of the junction. The junction of a standard platinum-rhodium couple may be inserted into a hole drilled in the junction formed by welding the material to platinum. This brings the junctions to the same temperature.

In the use of platinum or platinum-rhodium for testing thermocouple materials, the wires are used a large number of times before checking or scrapping. Base-metal thermocouple wires used for testing similar materials should not be used more than once if the highest accuracy is required, because there is a slight change in these materials when heated to a high temperature and if they are used repeatedly, the wires become inhomogeneous. The procedure then is to select a coil of wire and test it for homogeneity by taking several samples from different parts of the coil, welding them all together, and measuring the emf between the various samples. If the coil is sufficiently homogeneous as found from such tests, one or more samples may be taken from it and the thermal emf determined as accurately as necessary by comparison with a standard, the emf of which against the standard Pt 27 is known. The average value for the thermal emf of the few selected samples from the coil against the standard Pt 27 will apply for the remainder of the coil with sufficient accuracy for most purposes. Any sample from this coil may then be used as a working standard * for testing similar materials. The accuracy with which the temperature must be measured depends upon the difference between the standard and the material being tested. In case of some materials that have been well standardized, the differences are small enough that an accuracy of 50 °C is sufficient. Seldom, if ever, should it be necessary to measure the temperature closer than 10 °C.

Table 7. Thermal Emf of Annealed Electrolytic Copper against NBS Platinum Standard Pt 27.

Temperature (°C)	Emf (μv)	Temperature (°C)	Emf (μv)
−200	−194	100	766
−150	−354	150	1265
−100	−367	200	1831
− 50	−242	250	2459
0	0	300	3145
+ 50	+340	350	3885

(b) At Low Temperatures. Annealed electrolytic copper is very uniform

Table 8. Average Temperature-Emf Relations of Various Thermocouple Materials Against Platinum for Applying Reference-Junction Corrections.

Temperature		Electromotive force					
(°C)	(°F)	Platinum-rhodium [1] vs. platinum (mv)	Alumel-platinum (mv)	Chromel-platinum (mv)	Constantan-platinum (mv)	Copper-platinum (mv)	Iron-platinum (mv)
−20	−4	−0.101	−0.27	−0.50	−0.64	−0.109	−0.39
−15	5	−0.077	−0.20	−0.38	−0.48	−0.084	−0.30
−10	14	−0.052	−0.14	−0.25	−0.32	−0.057	−0.20
− 5	23	−0.026	−0.07	−0.13	−0.16	−0.029	−0.10
0	32	0.000	0.00	0.00	0.00	0.000	0.00
5	41	0.027	0.07	0.13	0.16	0.030	0.10
10	50	0.054	0.14	0.26	0.33	0.060	0.19
15	59	0.082	0.20	0.40	0.50	0.091	0.28
20	68	0.111	0.27	0.53	0.67	0.124	0.38
25	77	0.141	0.34	0.66	0.84	0.158	0.47
30	86	0.171	0.41	0.79	1.01	0.193	0.57
35	95	0.201	0.47	0.93	1.18	0.229	0.67
40	104	0.232	0.54	1.07	1.35	0.265	0.77
45	113	0.264	0.60	1.21	1.52	0.302	0.87
50	122	0.297	0.67	1.35	1.69	0.340	0.97

[1] These values apply for either 10- or 13-per cent rhodium.

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* Working standards of chromel and alumel prepared in this way, with certificates giving the thermal emf of the individual samples against the standard Pt 27 may be procured from the National Bureau of Standards.

Table 9. Summary of Methods and Accuracies Obtainable in Calibrating Thermocouples.

Type of thermocouple	Methods of calibration	Temperature range (°C)	Calibration points	Accuracy at observed points (°C)	Method of interpolating	Uncertainty in inte lated values (°C)
Platinum-10% rhodium	International Temperature Scale, fixed points.	660 to 1063	Freezing point of Sb, Ag, and Au.	0.2	*Equation:* $e=a+bt+ct^2$	0.2
Platinum-rhodium [1]	Fixed points	0 to 1500	Boiling point of water, freezing point of Sn, Pb, Zn, Sb, Ag, and Au.	0.2	Difference curve from reference table.	0.3 to 1100 and 2 at
	NBS standard samples, fixed points.	0 to 1500	Freezing point of Sn, Zn, Al, and Cu.	0.2	do	0.5 to 1100 and 2 at
	Comparison with standard couple.[1]	0 to 1500	About every 100 °C	0.5	Any	1 to 1100 and 2 at
	do	0 to 1500	About 600 and 1200 °C (or more points).	0.5	Difference curve from reference table.	1 at 1100 and 3 at
Chromel-alumel	Comparison with standard couple.[1]	0 to 1200	About every 100 °C	1	Any	2
	do	0 to 1200	About 500, 800, and 1100 °C (or more points).	1	Difference curve from reference table.	3
	Comparison with standard resistance thermometer[2] or at fixed points.	0 to 350	About every 100 °C	0.1	do	0.5
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60 °C	0.1	do	0.5
Iron-constantan	Comparison with standard couple.[1]	0 to 750	About every 100 °C	1	Any	2
	do	0 to 750	About 100, 300, 500, and 750 °C	1	Difference curve from reference table.	3
	Comparison with standard resistance thermometer[2] or at fixed points.	0 to 350	About every 100 °C	0.1	do	0.5
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60 °C	0.1	do	0.5
Copper-constantan	Comparison with a standard resistance thermometer[2] or at fixed points.	0 to 300	About every 100 °C	0.1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Comparison with a standard resistance thermometer.[2]	0 to 100	About 50 and 100 °C	0.05	*Equation:* $e=at+bt^2$ or difference curve for reference table.	0.1
	Fixed point	0 to 100	Boiling point of water	0.05	*Equation:* $e=at+0.04\,t^2$	0.2
	Comparison with a standard resistance thermometer.[2]	0 to −190	About every 60 °C	0.1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Fixed points	0 to −190	Sublimation point of CO_2 and boiling point of O_2.	0.1	Difference curve from reference table.	0.3

[1] Either 10- or 13-per cent rhodium.

[2] In a stirred liquid bath.

in its thermoelectric properties and is often used as a standard for thermoelectric testing at temperatures below 300 °C. The thermal emf of other materials against either copper or platinum may be determined very accurately by using a stirred liquid bath or fixed points. The steam point is an excellent one for this purpose.

Table 7 gives the thermal emf of annealed electrolytic copper against National Bureau of Standards standard Pt 27 and may be used to convert values of the thermal emf of any material against one of these standard materials to values of emf of the same material against the other standard material.

4. Reference-junction Corrections

It is not convenient for everyone to obtain the same reference-junction temperature in determining the emf of the various thermocouple materials against platinum and, therefore, corrections must be applied to arrive at values for a common reference-junction temperature. The method of applying these corrections is the same as that discussed under the testing of thermocouples. The average temperature-emf relations for the various thermocouple materials against platinum are given in Table 8 and may be used for making reference-junction corrections.

In comparing two samples of a similar thermocouple material at high temperatures, it is not necessary to measure or control accurately the temperature of the reference junctions. The emf developed by two samples of platinum-rhodium, even the 10 against the 13-per cent rhodium alloy, is practically independent of the temperature of the reference junctions between −20 and +50 °C. In all other cases, with the possible exception of iron, the emf may be taken as proportional to the difference between the temperatures of the two junctions, and when the emf is small, the corrections for the temperature changes of the reference junctions are negligible. In comparing two samples of iron, the emf developed is changed more by changing the temperature of the reference junctions than by changing that of the hot junction by the same amount, for example it was observed (in one case) that the emf (320 μv) developed by two samples of iron when one junction was at 600 °C and the other at 25 °C changed by 0.1 μv for each degree change in the temperature of the hot junction and 1.4 μv for each degree change in the temperature of the reference junctions.

VIII. Accuracies Obtainable

The accuracies obtained in calibrating the various types of thermocouples by different methods and the uncertainty in the interpolated values by various methods are given in Table 9.

These accuracies may be obtained with homogeneous thermocouples when reasonable care is exercised in the work. More or less accurate results can be obtained by the same methods. In the case of chromel-alumel and iron-constantan couples at low temperatures, the accuracy given in Table 9 is limited by the uncertainty in interpolated values. However, this uncertainty can be greatly reduced by observing the emf of the couples at more points. The accuracy obtained with copper-constantan couples at low temperatures is usually limited by the emf measurements and in such cases the accuracy may be improved by employing a number of couples in series (multiple-junction couples).

When it is desired to test a thermocouple and leads or thermocouple, leads, and indicator as a unit by any of the methods described in the preceding sections, no additional difficulties are encountered.

Table 10 gives the uncertainty in the thermal emf measurements of various thermocouple materials against the standard Pt 27 produced either by an uncertainty of ±2 °C in the temperature measurements when platinum is used as a working standard, or by an uncertainty of ±10 °C in the temperature measurements when the material is compared with a working standard of the same material, the emf of which has been previously determined against the standard Pt 27 to the equivalent of ±2 °C. In the former case the uncertainty in the emf measurement is proportional to the uncertainty in the temperature measurement, whereas in the latter case it depends only slightly upon the temperature measurement provided the emf of the working standard against the standard Pt 27 is known to the same accuracy.

Table 10. Uncertainty in the Determination of the Thermal Emf of Thermocouple Materials Against Platinum.

Material	Uncertainty in electromotive force (mv)
Platinum	----
Platinum-10 per cent rhodium	0.03
Platinum-13 per cent rhodium	.03
Alumel	.02
Chromel	.07
Constantan	.10
Iron	.03

The following services are provided by the National Bureau of Standards for fees covering the cost.

(1) Thermocouples are calibrated and certified as accurately as the conditions of use and the homogeneity and stability of the wires justify. The accuracies given in Table 9 have been found to meet most needs.

(2) Indicators used with thermocouples are calibrated separately or in combination with a particular thermocouple.

(3) The thermal electromotive forces of thermocouple materials against the standard Pt 27 are determined and the results certified to the limits justified by the material.

(4) Standard samples of thermocouple materials are distributed with certificates giving the thermal electromotive forces of the individual samples against the standard Pt 27. The materials being distributed at present are alumel and chromel P.

(5) Standard samples of metals are distributed, each with a certificate giving the value of the freezing point. The freezing-point metals being distributed at present are tin, lead, zinc, aluminum, and copper.

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Chapter 3
Education

An Industrial Course in Temperature Measurements

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Industrial applications of temperature measurement have increased rapidly both in number and in importance in the past twenty years, but the control of temperatures of industrial processes within the close limits now set in many fields is relatively a new art. Together with this increase in use, there has been a development in instrumentation to keep pace with it, and temperature-measuring equipment has advanced in dependability, in adaptability, and at the same time in complexity. In this country millions of dollars are being expended annually for the purchase of apparatus for the measurement and control of temperature by electrical methods. The instrument expert, who is becoming a very necessary member of the personnel in large plants, such as steel mills and oil refineries, is trained to install and maintain the temperature devices which are ensuring uniform products, and is safeguarding lives and property.

Adequate training in our technical schools for men to fill such positions is almost entirely lacking, and the men who are now doing the work have gained their knowledge on the job and seldom have any extensive training in temperature measurements outside the limited range of instrumentation with which they are in immediate contact.

I am not an advocate of more specialization in engineering; on the contrary, it is my belief that much more emphasis should be placed on the fundamentals of physics, mathematics and chemistry. Speaking as a physicist, I would wish to see every engineer required to pass courses in classical physics extending over at least two, and better, three years of his course of study, in which a definite attempt is made to correlate the various branches of the subject, and to emphasize practical applications. He should start out, not as a proficient electrical or mechanical engineer, which he will not be in any case until he has found a job and learned how to fill it, but as a well-balanced candidate for practical training in the work that he may secure. But naturally during his technical course, he will devote himself to the particular branch of engineering which most appeals to him, gaining an intimate acquaintance with electrical, mechanical, or chemical subjects, while not remaining entirely unfamiliar with the others, because of his courses in physics and chemistry.

In suggesting the desirability of a more adequate presentation of temperature measurement in our schools, my idea is not specialization, but the provision of an opportunity of studying a subject which is almost equally important to the chemist, the metallurgist, and the power-plant engineer, and for which a good understanding of electrical circuits and of physics is required. It is evident that no one department of the engineering school can claim the subject as its own, and it is perhaps for this reason that it is not more generally taught. It might be entrusted to the physics department, but there the practical side of the subject is not likely to be emphasized, and its presentation will probably be confined to a small portion of a course in heat. The problem is probably one for which local conditions and the availability of a competent man to organize such a course must be the deciding factor. If, for example, the Department of Metallurgy has a man who is well trained in temperature work, he might be encouraged to widen his field to include the problems of the chemist, those of heating and ventilation, of the steam engineer, etc., and to present a course which could be elected by students in any field of engineering. Such a course should be made to include recent equipment and methods as well as the older ones, and at least a reading knowledge of modern industrial instrumentation.

The scarcity of technical graduates with such a training has made it necessary for the Leeds and Northrup Company to provide a means of supplementing the education of young men whom it employs for sales work. For the past two or three years, it has also been found desirable to give this course to some technical graduates employed to take up work in the Engineering Department.

This company, like many other industrial concerns, has made a practice of recruiting its technical and sales forces from the graduating classes of the colleges and universities. These young men have been selected not only on the basis of their scholastic attainments, but also with some reference to their extra-curricular activities, particularly in the direction of self-support. Up to 1935 they were brought into our laboratories fresh from college and given a brief introduction to the business and to some shop and laboratory operations, together with training in the adjustment of instruments. The new men who were to take up selling were then put in the field under the tutelage of our experienced men, and got the rest of their training in the school of hard knocks.

We became dissatisfied with the results of this type of training, as too many opportunities were being missed due to lack of a real understanding of the capabilities and limitations of the instruments which were being recommended to purchasers, and an inability to recognize possibilities in new fields. Consequently, in 1935, provision was made for establishing a well organized training course to give technical graduates a thorough grounding in the theory of the instruments that they were to sell, together with a facility in operating and servicing them.

The great diversity of the instruments produced makes it hopeless for any individual to attempt to master all of them, and it was therefore necessary to provide five courses with temperature measurement common to all. These are:

(1) *Electrical:* Power plant, communications, laboratory instruments.
(2) *Chemical:* Electrolytic conductivity, hydrogen ion, gas analysis.
(3) *Mechanical:* Flow meters, recorder mechanisms, relays, etc.
(4) *Metallurgical:* Heat treating, carburizing, electric furnace design, etc.
(5) *Temperature:* Thermocouples, resistance thermometers, radiation pyrometry, temperature control, etc.

The planning and conducting of the course was put in the hands of the Research Department for various reasons. Under the former system, the experience gained in the production shops was fragmentary; there was a tendency to keep the student on a particular job much longer than was needed to give him an adequate knowledge of it, in order not to interfere with production; processes of manufacture gave little insight into the design and uses of the instruments. In the Research Department the students could be entirely separated from production, and given fundamental instruction by men who had had a considerable experience in teaching in universities; apparatus and laboratory space were available in the Research Laboratories: and, further, the research men had a definite interest in securing more intelligent coöperation in introducing new apparatus to the users in the field.

The course specializing in temperature is the one which is to be described, and is typical of the others. The work as laid out covers from nine months to a year, eight hours a day, five days a week, with outside reading encouraged but not required.

The first week or more is devoted to a rapid survey of the field by intensive reading of available textbooks—most of them inadequate—the Bureau of Standards Technologic Paper 170, and the 1919 Symposium on Pyrometry, as well as commercial descriptive material. Then experimental work is started, studying thermocouple materials and calibrating various couples, at the same time acquiring familiarity with various types of potentiometers of the indicating variety.

The recording potentiometer and controller are next taken up, and some weeks are spent in studying the various mechanisms and electric circuits involved: tearing down and reconstructing a recorder, and computing circuit constants for some particular application, and then wiring and calibrating the instrument to check the computation.

Resistance thermometry follows, and both precision and recording thermometer bridge circuits are studied and used.

Then follows a detailed study of radiation pyrometry with emphasis on both optical and total radiation methods. Both types are calibrated by approved methods, emissivity corrections determined for various surfaces, sources of error pointed out, etc.

The purely temperature part of the course ends with three or four weeks devoted to theoretical study and practical application of temperature control by both electrical and pneumatic methods, using a laboratory set-up which simulates control problems encountered in the field.

In order to give the student a degree of familiarity with lines of the company business which he may encounter in the field, but with which he is not expected to be as fully familiar as with his chosen line, he is given a brief course in metallurgy, including heat treatment, hardening practice, and electric furnace construction, and in miscellaneous non-temperature equipment, such as a. c. and d. c. bridge methods, flow meters, and various branches of the electrochemical field—electrolytic conductivity, pH measurements and gas analysis by thermal conductivity methods.

In addition to this work there is a course of lectures, covering company organization and policies, the functions of the various departments, and also some of the fundamental elements of instrumentation and the component parts of electrical instruments, such as resistance coils and slidewires, capacitors, insulating materials, etc.

Finally two or three weeks are spent in learning to repair and service instruments to be encountered in the field, under the instruction of an expert service man.

The Sales Department now takes the student in charge and usually assigns him to serve as assistant to one of its sales engineers, to work on problems which are not of a routine nature, particularly in the introduction of new instruments or new applications of old ones. Or he may serve for a year on service work in the field. He is usually not employed as a salesman until he has worked in the field in other capacities for a year or more.

Naturally such a training course is expensive and consumes much time of the Research Department staff which would otherwise be devoted to development work, but the results have more than justified it. The "graduates" of the courses are scattered across the country from Boston to Los Angeles, and have fitted into the sales organization without friction, carrying with them a most wholesome spirit of coöperation between Research and Sales. The familiarity with research problems and methods which they have acquired incidentally during their training is of value to them in their later work and they are more free in coming to us with their technical problems than if they were not so well acquainted with the research men who were their instructors.

One of the most encouraging manifestations of this phase of our experience has been the frequency with which they have furnished definite and often practicable suggestions for new means to meet the difficulties which they have encountered.

It is not suggested that a technical school could or should attempt a course in temperature engineering along the lines that have been indicated, nor that what has been described is a complete coverage of the field. No time is devoted to expansion and pressure types of thermometers; the fields of calorimetry and heat conduction are not touched, and, except in an incidental way, no time is devoted to instruments not of our own manufacture. We attempt to prepare the students to be as useful as possible to us. An educational institution would not be justified in narrowing the field as much as we have done, nor in devoting as much time to some types of instruments as we have found advisable. No criticism is intended of the excellent courses in temperature measurement which are offered in a very few of our technical schools, but it is to be hoped that there may be a considerable increase in the number of institutions which make such instruction available.

The Teaching of Pyrometry in Technical Schools

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At a symposium on Pyrometry held in Chicago twenty years ago Professor G. V. Wendell presented a paper with the foregoing title. It might now be significant to note briefly in what respects progress has been made in the field of Temperature Measurement. Unlike nuclear physics, which has experienced revolutionary advances in this period, pyrometry had already attained maturity in 1919.

The following random achievements are representative of advances made in this period. Liquid helium was frozen by Keesom in 1926 for the first time. In 1927 thirty-one countries agreed to accept an International High Temperature Scale. The freezing points of several of the noble metals have been determined at the National Bureau of Standards. Temperatures higher than any hitherto attained, in mass, have been produced by means of the high-frequency induction furnace. Striking experiments on the adiabatic demagnetization of paramagnetic substances have yielded temperatures close to the absolute zero. Yet it is perhaps safe to say that little advance or fundamental change has been made in the basic theory underlying the operation of devices for the measurement of temperature.

During this same interval there has been a tremendous expansion in the use of equipment for the precise measurement and control of temperature in industrial processes. This demand has given a constant impetus to the development of more accurate and versatile equipment. Because of accurate control of temperature, many products are now available whose existence otherwise would be impossible, and others now have properties unattainable when inadequate control existed. It is undoubtedly true that few articles are produced that do not require one or more carefully controlled thermal operations at some stage in their fabrication.

This widened industrial usage has created a demand for technicians trained in the use and application of thermal equipment. Students whose fields of specialization are industrial physics, chemical engineering, ceramics, metallurgy, and perhaps electrical and mechanical engineering have a definite need for training in this field. To meet this need, an adequate course should be presented either in the department of physics or the department of engineering, as determined by local conditions. The course should do more than familiarize the student with the commercial instruments on the market. It should present the fundamental principles underlying the construction and operation of various devices for the production, measurement, and control of both high and low temperatures, and should deal with the limitations, the reliability and the relative accuracy of such equipment. The aim should be to develop resourcefulness such that the graduate could meet any problem with intelligence and confidence.

Such a course might reasonably consist of lectures with cognate reading in texts and periodicals, supplemented by the working of problems and much time spent in the laboratory. The latter is invaluable. If continued for one semester, a one-hour lecture period together with a three-hour laboratory period should be sufficient. The prerequisites should certainly include a year's course in college physics. The completion of a course in electrical measurements would be helpful, but not compulsory.

Since in the natural process of the survival of the fittest, certain devices are little used in practice while others have wide application, it is reasonable that the emphasis in instruction be similarly placed. It has been the experience of the writer that a set list of experiments in which a rigid routine is to be followed is neither wholesome nor desirable. It is better if the student can be made to feel that every experiment is an independent investigation. Originality leading to better performance of the equipment or more accurate results should be encouraged. This will result in greater interest and enthusiasm on the part of the student, and the course will thus continually be in a state of evolution.

Experiments of various types will be performed. These may have as their aim (a) the qualitative demonstration of a physical principle, such as the Peltier effect or Thomson effect; (b) the calibration or the determination of the limit of accuracy of some piece of equipment, such as an optical pyrometer; (c) the precise determination of some physical constant, such as the freezing point of a metal or a transition point in a metal; or (d) the development or assembling of equipment for some particular, unusual project.

The following list of experiments is in no sense to be regarded as complete, but rather as suggestive of the types of procedure that may be carried out.

Thermocouples

Exp. 1: Demonstrate the existence of the Peltier effect and the Thomson effect.

Exp. 2: Construct an iron-constantan thermocouple and calibrate by means of established fixed temperatures. Fit a mathematical equation to the temperature-emf relationship.

Exp. 3: Using a large number of metals and a rotary switch, obtain the emf of each metal against constantan, as the temperature of the common hot junction is increased.

Exp. 4: Study the effect of changing the reference junction temperature for both base and noble metal couples.

Exp. 5: Compare the effectiveness of deflection and null type indicating instruments.

Resistance Thermometers

Exp. 1: Using established fixed temperatures, calibrate a platinum resistance thermometer. Fit an empirical equation to the data. Determine the constant in the Callendar correction formula.

Exp. 2: Study various methods of compensating for lead wire resistance.

Optical Pyrometers

Exp. 1: Using a standardized broad-filament incandescent lamp, calibrate optical pyrometers of various types. Can the data be accommodated by a simple mathematical relationship?

Exp. 2: Extend the range of an optical pyrometer by using (a) an absorbing screen or (b) a rotating sectored disc. Express the coefficient of absorption of the material of the absorbing screen and then measure the temperature of the sun.

Exp. 3: Determine the emissivity of various surfaces, (a) using a thermocouple for the true temperature and an optical pyrometer for the apparent temperature, or (b) using a Mendenhall optical wedge.

Exp. 4: Demonstrate errors due to lack of focus, reflectivity of the source, or other causes.

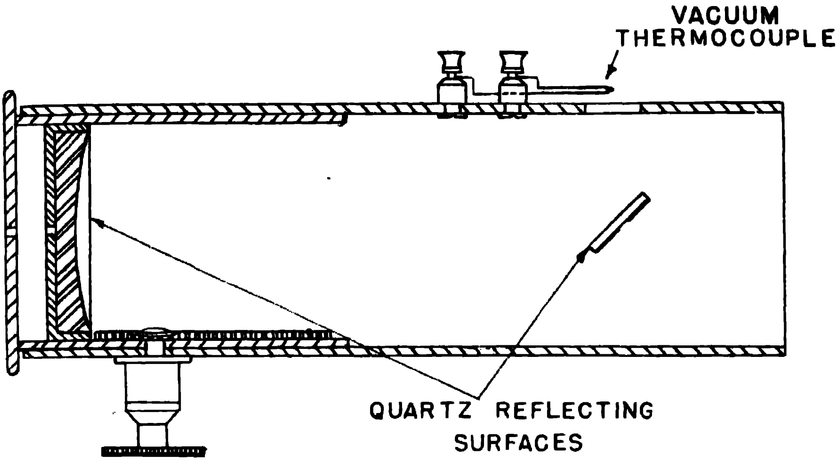


Fig. 1. Infrared pyrometer residual rays.

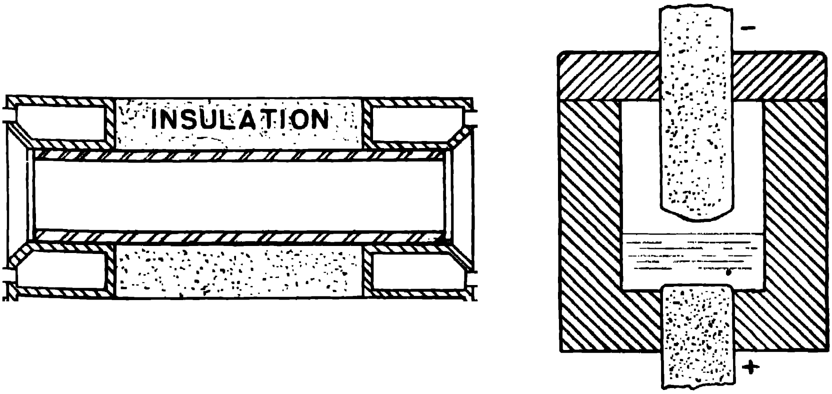
Radiation Pyrometers

Exp. 1: Using sources at fixed known temperatures, calibrate various total radiation pyrometers. Show the validity of the fourth power law.

Exp. 2: Determine the total normal emissivity of various surfaces.

Exp. 3: Study the effect on the indication of the pyrometer of certain interposed absorbing layers.

Exp. 4: Construct and calibrate an infrared pyrometer, making use of reflections from aluminized surfaces or of the selective reflectivity (reststrahlen) from crystalline surfaces. Fig. 1 shows such a device using quartz surfaces. When used with a sensitive galvanometer or with an insensitive galvanometer if the surfaces are aluminized it may be employed to measure the temperatures of surfaces down to less than 100 °C.



b. Carbon rod conductance furnace　a. Siemens arc furnace

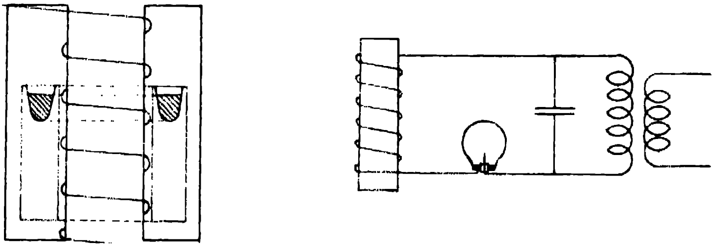
Fig. 2.

Recorders and Controllers

Exp. 1: Make an assembly of some electrically operated furnace, so that the temperature is indicated and controlled automatically at a predetermined value.

Furnaces

Exp. 1: Construct an electric furnace of some type from improvised material and observe its efficiency and limitations. Figs. 2 and 3 are representative of such furnaces that can be built at small expense in the student shop from materials usually available around a laboratory. As shown, these are: Fig. 2, (a) a Siemens Arc, using an iron pail, a large carbon rod and fireclay; (b) a hollow carbon rod with water-cooled ends and stepdown transformer; Fig. 3 (a) a low-frequency induction furnace from transformer iron, fireclay and copper wire; and (b) a high-frequency induction furnace using a mercury spark gap and an old x-ray transformer. Assembling a device similar to these stimulates the ingenuity of the student and is most instructive on such matters as power measurement, temperature limitations, and heat transfer.



a. Low-frequency induction furnace b. High-frequency induction furnace

FIG. 3.

Fundamental Constants

Exp. 1: Determine the melting point or boiling point of some substance.

Exp. 2: Evaluate the transition temperatures in pure iron.

Exp. 3: Determine the value of, (a) the constant (σ) in the Stefan-Boltzmann law and (b) the constant C_2 in the Wien or Planck laws of heat radiation.

It may be permissible and fitting to mention a few details regarding experiments of this type. There is a definite satisfaction in being able to determine precisely the value of a fundamental constant of nature. While these radiation constants have been evaluated by painstaking investigations involving elaborate expenditures of equipment and time, it is possible by rather simple manipulations to arrive at values almost equally good.

The Planck constant may be found by an arrangement such as that shown in Fig. 4. This consists of an optical pyrometer, monochromatic for the wavelength λ, a standard temperature source and a rotating sectored disc which may or may not be interposed between the pyrometer and source. All that is needed is to observe the true temperature of the source, T, and the apparent temperature, T', viewed through the rotating sectored disc, whose ratio of open to total space is R. The fundamental constant is readily shown to be:

$$C_2 = \frac{\lambda T T' \log_e 1/R}{T - T'}$$

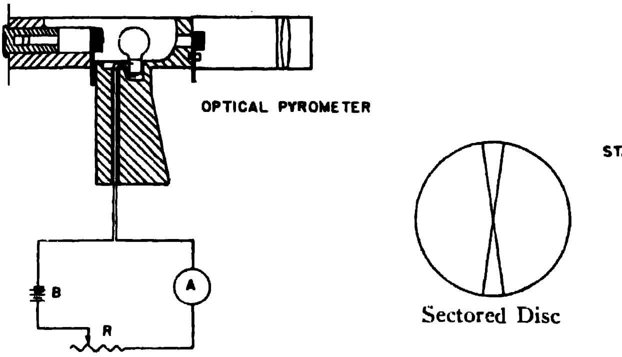


Fig. 4. To determine the Wien constant, c_2.

For the Stefan-Boltzmann constant (σ), the arrangement shown in Fig. 5 is employed. This consists of a blackened hollow metal sphere equipped with an electric heating coil at its center and a thermocouple in a small drill hole at the surface. The sphere hangs in an evacuated enclosure whose walls are maintained at a constant temperature. Observations are made of the input power and the temperature of the sphere for an equilibrium condition. Such an experiment not only yields a very fine value for the radiation constant, but it gives valuable experience with evacuating systems, McLeod gauges, and the precise measurement of electrical power.

Conclusion

It is perhaps futile to expect that exposure to any course, however well it may be planned and carried out, will universally result in the type of graduate hoped for. Certain individuals having simply gained an acquaintance with various instruments will at best be qualified merely as operators. On the other hand there will be many who, having profited by the contacts and the experiences gained in a course of this kind, and the opportunity and necessity of demonstrating initiative, will be enormously benefitted. They will have acquired a confidence and soundness of judgment that will enable them to cope successively with whatever subsequent problems may

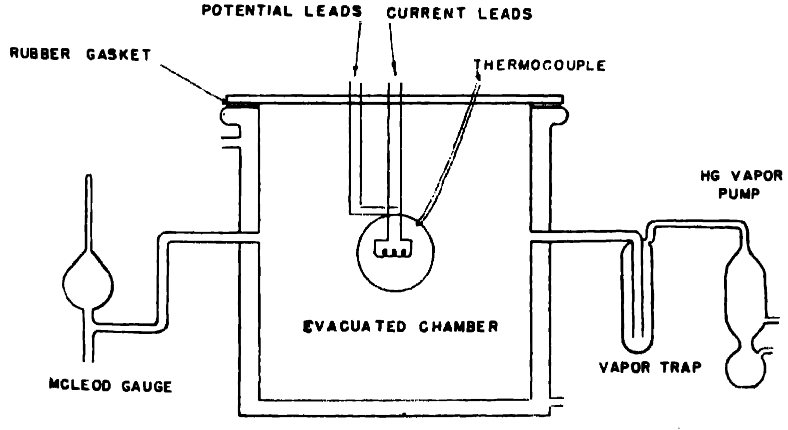


Fig. 5. To determine the Stefan-Boltzmann constant.

The Education of a Pyrometrist

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Ideas concerning what constitutes an education, and concerning whose interests it is expected to serve, vary so widely that I am going to try to avoid inconsistencies and sweeping generalizations by considering a concrete case. Let us imagine ourselves in the position of the general superintendent of a steel plant and try to see what qualities he would like to find in a pyrometrist whom he is about to employ.

The Operating Pyrometrist

First, what is the job to be done? It has not been many years since the plant superintendent would not even have known what is meant by the term *pyrometrist.* Though temperature is one of the two all-important variables in steelmaking, it was measured not with instruments but with the human eye, which by the way is not at all a bad pyrometer; it is better, indeed, than some pyrometric instruments now for sale. But increasing complexity in the processes—for example, the heat-treating of steel where it is out of sight—and, even more, the introduction of automatic controls to avoid troubles due to human carelessness and forgetfulness, have brought pyrometers into all parts of the iron and steel plant. Some of these instruments, such as the optical pyrometer, require an observer. Some, though they make an automatic record, must be set at the proper point at the proper time. They all require routine maintenance, such as the replacement of dry cells, the oiling of motors, and the cleaning cf lenses. They all require calibrating to insure their correctness. Of greatest importance, they all require special servicing, tuning, and adaptation to the process, in order to insure that the readings or the records mean something. Now that the number of pyrometric instruments in the big plants is mounting into the hundreds, a full-time job exists for at least one man and sometimes several men just to keep the instruments going satisfactorily.

I could tell you of plants outside the steel industry in which this simple fact is not yet appreciated and in which the management seems to have an ill-defined impression that once an automatic recorder or controller has been installed, no further attention need be paid to that part of the operation or to the pyrometer connected therewith. But these tales would be aside from our present subject. We want a pyrometrist: how shall he be selected?

Reminding you that we are trying now to see the case through the eyes of the plant superintendent, I must record the conviction that the pyrometrist's education is a matter of secondary importance, that what counts most is the group of native qualities which he has inherited from the last three or four generations of his ancestors. The boy who loves to make wheels go round, who made his own radio sets in the 1920's, who buys a $15 Ford wreck and makes it run again, will be the man we want. His secondary school education? Four years of Latin is as good as anything; if the mind is alert it can always be improved by the training in analysis and deduction and the experience in changing from one kind of expression into another, that is furnished by a study of the dead languages. Mathematics he should have, of course, for its training in logical thinking. For the rest, any kind of entertainment he prefers, from astronomy to zoology.

College education? Unnecessary, but desirable, mainly because if a lasso is thrown into a college crowd, the chances of getting a man with the right instincts to make a good pyrometrist are much better than if a lasso is thrown into a mass meeting in a public square. The superintendent will not forget, also, that it is possible to secure desirable training or coaching in an institution for advanced education, even though that is not the institution's primary purpose. If the college, technical school, or night school has good physical equipment, it will possess a potentiometer with some thermocouples, some automatic recorders of both the millivoltmeter and the potentiometer type, automatic control devices such as relays and valves, and perhaps optical and radiation pyrometers. Departments of mechanical and electrical engineering, rather than a physics department, are most likely to have the desirable equipment and to permit it to be used. Civil engineering, ceramics and chemistry are not likely to offer the future pyrometrist anything very useful. Some coaching in shop-work is particularly valuable. One specialty that may best be sought in the physics department, however, is work with electron tubes and photosensitive cells. These devices are coming into increasing use in pyrometry; but the subject is new and in the stage where much more is being learned than is being told.

Another useful source of coaching and training is the factory of the pyrometer manufacturer. Most of the manufacturers have made provision to receive the pyrometrist in the instrument-making plant, and to show him how the instruments are made, tested and best maintained in working order. The course of instruction may cover several days or weeks.

The Research Pyrometrist

What the country needs is more skepticism. This is just as true in the field of pyrometry as it is in politics. It is only natural for the observer to believe that a smooth-working, well-oiled, noiseless instrument in a stream-lined case must be telling the truth, particularly if it has a clear, sharply drawn scale and an index that permits it to be read with a precision of 1 °F. When such an instrument, attached to a control mechanism, draws a red line on the chart so straight that it could hardly be improved upon with a straightedge and ruling-pen, it is repugnant to reflect that maybe the metal whose temperature purports to be recorded is actually much colder or hotter than indicated, and is furthermore fluctuating through a range that would look very bad on the record that goes on file in the main office. Yet investigation shows that such is often the case.

Thus we need in the plant another kind of pyrometrist, one who, when the operating manager and his loyal pyrometric helper point with pride to a beautifully consistent record or table of readings, will have the independence to inquire skeptically, "How do you know?" In self-defense, they can conduct the skeptic to the pyrometry laboratory and prove that the thermocouple is correct, the electrical recording instrument perfect, the optical pyrometer reading true brightness-temperature as calibrated against a standard source of light. After admitting that the instrument is recording the true temperature of the thermocouple junction, the skeptic can still ask the embarrassing question, "How do you know that the junction is at the same temperature as the steel?"

This inquisitive pyrometrist, whom we may call the "research" type for lack of a better term, and of whom there should be at least one for every five or ten of the variety first described, has other duties. If he finds that the pyrometer is not telling the truth, or that the pyrometric controller is not operating the furnace as efficiently as a man could operate it, it is up to him to make the instrument do better, or to devise a better instrument. He may be able to work more efficiently as a special fuel engineer or a research metallurgist in the plant, or as a research and development man in an instrument company. One attribute that he must lack is complacency. As for his positive qualities, it will not be out of place to review here the classification of the instincts of the investigator that Professor W. M. Wheeler presented years ago; no better classification is known to me.

Wheeler,[1] after a lifetime of study of ants and other social insects, and after reflecting upon their qualities as compared to those of mankind, concluded that the scientist or investigator is driven by eight recognizable instincts, of which four are individual and four social. The first four are

(1) Curiosity,
(2) Hunting.
(3) Collecting,
(4) Workmanship;

While the social instincts are

(5) Emulation,
(6) Communication,
(7) Appreciation,
(8) Coöperation.

The instinct of curiosity need not be particularly strong in our research pyrometrist, though it should be present to some degree. He is not only concerned with getting at the truth as a professional duty; he is also curious to know just what is going on inside the pyrometer tube or the furnace, particularly if something new and mysterious has happened to interrupt the record or change the controlled temperature.

The hunting instinct, on the other hand, should be strong. It is the drive that leads individuals to undergo all sorts of hardships for the sake of tracking down something elusive, and overcoming it if it seems dangerous. Observe the triumphant tone with which the pyrometrist announces, "I spent half a day fighting that bad contact in the relay and I've got it licked."

The collecting instinct, manifested in its least intelligent form in the postage-stamp collector, and existing as a very strong drive in the botanist and the mineralogist, may be completely absent in our pyrometrist.

Extremely important is the so-called "instinct of workmanship, craftsmanship or contrivance." It is what drives a bird to build a nicely rounded and smoothed and even a decorated nest when a pile of grass and twigs would be sufficient. It prevents our pyrometrist from being satisfied with an instrument or method that is just "good enough."

The social instincts, too, must be sought in our pyrometric candidate. First, emulation; when fed by an occasional opportunity to see other men's pyrometers and to compare notes professionally, it brings about improvements in application of the pyrometric art on the part of all who participate.

Secondly, the instinct of communication. This is one that the employer can easily do without, but it is an instinct whose intensity in the research man often goes unperceived or misunderstood by the industrial executive, in whom this instinct is likely to be weak or absent. In a competitive industrial system it is a handicap, for there is no sense in spending money to learn something new and valuable and then blandly revealing it to competitors without asking for any compensation. Nevertheless, its existence must be recognized and taken into account, for it has led more than one genius in research or invention, whose work would have been worth that of a score of us plodding experimenters, to stay in a university where he could talk freely with his fellows and refuse employment in an industry where he must keep silent.

Closely allied to communication is the third social instinct, the craving for sympathy, understanding, appreciation and recognition. Unlike the communication instinct, it is probably a good trait for the pyrometric candidate to have. For example, it is a strong influence in getting work out of an individual who may have a good brain but is handicapped by such failings as indolence or indecision. It is more easily handled than the instinct of communication, because a few properly spaced promotions, titles, citations, medals or the like are usually sufficient to satisfy it.

The last instinct on the list, coöperation, is very necessary in industrial research and very weak in the best research men. New information and new devices are valueless unless they can be translated into action in the every-day operations of the plant. This requires ability to take into account the other man's point of view, to recognize that the operator knows some things by daily experience and observation which the research man may not even suspect, and to gain the operator's confidence and wholehearted backing. A research or development group usually must strike a compromise by matching each non-coöperative investigator with an able and understanding coöperator, who may not be a genius at invention or discovery but can get things done in the plant.

The desirable education of our research pyrometrist is limited only by the time that he can afford to devote to it. As he may be in the group from which the management is subsequently selected, he may do well to get his secondary school education in a school which devotes itself to laying a broad foundation for subsequent university scholarship, unhampered by the often narrow educational ideas of local public school boards, who can see the usefulness of pyrometrists of the first type but not of the second. In college and technical school he should have plenty of mathematics and physics, particularly the fundamental principles of physics, with experimental illustration. I should like to see him given more chemistry than most physicists have had a chance to absorb. Though James Phinney Munroe may be right in declaring that "the curse of American scholarship and of American education is the Ph. D.," the experience in genuine research that every reputable institution requires as a prerequisite for this degree is a very necessary part of the education of our research pyrometrist. I believe, however, that this "prolongation of infancy," as John Fiske called it, could well be interrupted by a year or two of experience in an industrial plant.

As specific subjects for pyrometric research there should be mentioned again electron tubes and photoelectric cells. Not all of us realize fully what a revolutionary opportunity we have in an instrument in which the negative electron is separated from its customary association with atoms and molecules, and subjected to control by electric, magnetic and thermal gradients. The speed of action of these devices is inconceivably high, and high-speed pyrometry is a field in which barely a beginning has been made.

The laws of radiation, especially of the infrared, should also receive much more attention. The energy radiated by even the white-hot objects in a steel plant is nearly all invisible and on the long-wave side of the spectrum. Radiational pyrometry provides the logically simple and direct way to measure the temperature of a warm or hot surface, and is an art that is now far behind other branches of pyrometry and thermometry.

When the pyrometrist accepts a job his education has only just begun; like the famed education of Henry Adams, the rest of it will consist mainly of things learned in the school of experience. The pyrometrist will learn that the most unpredictable and, at the same time, most important variables in the management of instruments are the human factors—the instinctive reactions, sensitivity, speed of action, and fatigue of the human mechanism; also such influences as prejudice, personal attraction and repulsion, and plant politics. One or another of these factors may completely mask the normal and expected action of a good optical pyrometer or temperature controller. Finally, on some occasion when he has done his professional best to design a set of pyrometric equipment that promises to accomplish the desired purpose, he will make the acquaintance of that disheveled old reprobate over whose portrait in a recent journal many a metallurgist is still chuckling: that famous though mythical Greek, Reciprocrates, about whom few technical men can speak without using a kind of profanity that would not look well in print.

In closing, let me remind you again that we have been looking at education with the practical eye of the plant superintendent. To show that there are other sides to the subject I shall confine myself to a quotation from President K. T. Compton, who, speaking at the installation of a new Director of Cooper Union in New York just a year ago, stated what appeared to be his own view of the function of a college: "a place where educational opportunity is offered under stimulating surroundings, and not an intellectual stock farm where the animals are fed and fattened for the market." You will therefore not take my brief contribution as the last word in how a teacher should educate a pyrometrist, or how a pyrometrist should educate himself, but merely as a bit of what the School of Business Administration likes to call "market research."

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Instruction in Temperature Measurement to Mechanical Engineering Students

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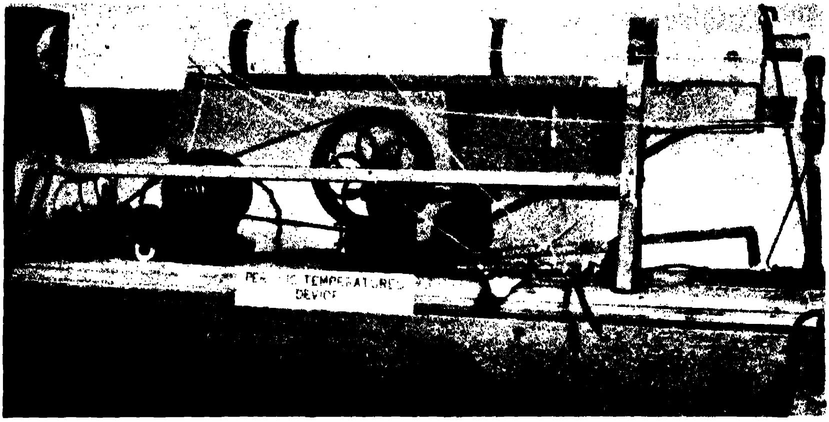
Introductory Remarks

Successful technical engineering requires a thorough knowledge of mensuration or the art of obtaining experimental data of known reliability. The fundamental measurable quantities are force, length, time and temperature, of which variables temperature is the most difficult to measure accurately. For this reason temperature measurements receive great emphasis in the undergraduate laboratory work of the mechanical engineering student. Instruction in this subject is given at the University of California in the second year Production Engineering Laboratory course and in the fourth year General Mechanical Engineering Laboratory course. In both courses the student is encouraged to become cognizant of the sources of error as well as familiar with the more common instruments and techniques of measurement.

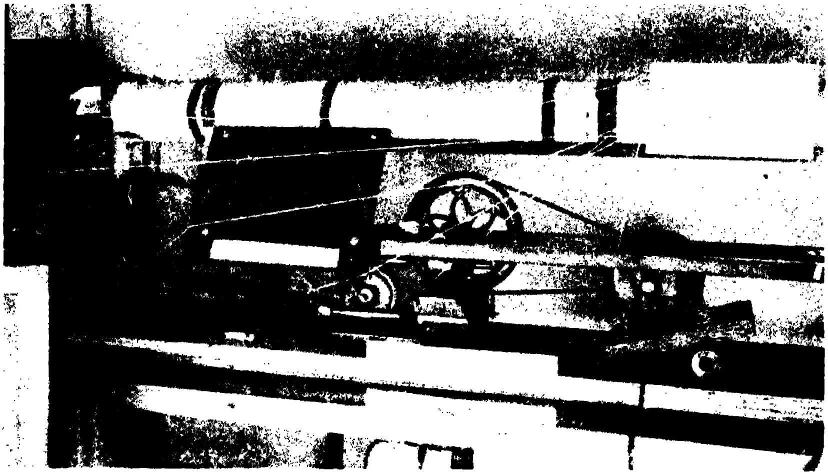
Since a large proportion of mechanical engineering experiments involve the measurement of temperature, it is possible for the student to become familiar with a variety of temperature-indicating devices without making temperature measurements the main subject of investigation in any one experiment. Realization of this benefit depends upon a proper selection of the instruments used in connection with the various experiments. The instruments selected should exemplify as many as possible of the several thermal effects available for thermometric purposes, (A. S. M. E. Test Code on Temperature Measurement), namely: change of linear dimensions and volumes, change of electrical resistance, variation of vapor pressure, development of thermoelectric potential and change of radiation intensity (both visible and infrared). For example, mercury thermometers are used on a Junkers calorimeter experiment, thermocouples on the test of a journal bearing and on heat-transfer tests, vapor-pressure instruments for condenser cooling water temperatures, an optical pyrometer for furnace temperatures. By a proper introduction of each of these devices as auxiliary to another experiment the student obtains a "speaking acquaintanceship" with the various instruments and their manipulation.

The formal study of temperature measurements is introduced by a lecture on the general topic of mensuration. In this lecture an attempt is made to analyse the indications of a general measuring device in terms of the following classification:

- Characteristics of the quantity being measured
  - Measurable effects of variation
  - Variations with time
- Characteristics of the instrument
  - Null or deflection type
  - Range and scale division
  - Intrinsic inaccuracy



Rear view



Front view

FIG. 1. Periodic temperature device.

  - Variance and sluggishness
  - Natural frequency
  - Damping
- Characteristics of the instrument station
  - Type of connection between instrument and point where variable is to be measured
  - Location of instruments with respect to extraneous effects

Mechanical resonance is demonstrated by a simple spring mass system driven through a crank and crosshead by a variable-speed motor. Examples are quoted during this lecture from the metering of various quantities such as pressure, force, time, speed and temperature. The experiments on temperature measurement follow in general the same outline.

Characteristics of Temperature

In beginning the study of temperature measurements an attempt is made to define temperature. Many engineering textbooks define temperature as a potential controlling heat flow. For example, Barnard, Ellenwood and Hirshfeld[1] use the following: Temperature is "the thermal condition of a substance which determines the tendency of this substance to give or receive heat from other bodies."

Roberts,[2] in writing of temperature measurements, defines temperature by the statement, "If a thermometer placed in contact with various bodies gives the same reading, we say that the bodies are all at the same temperature."

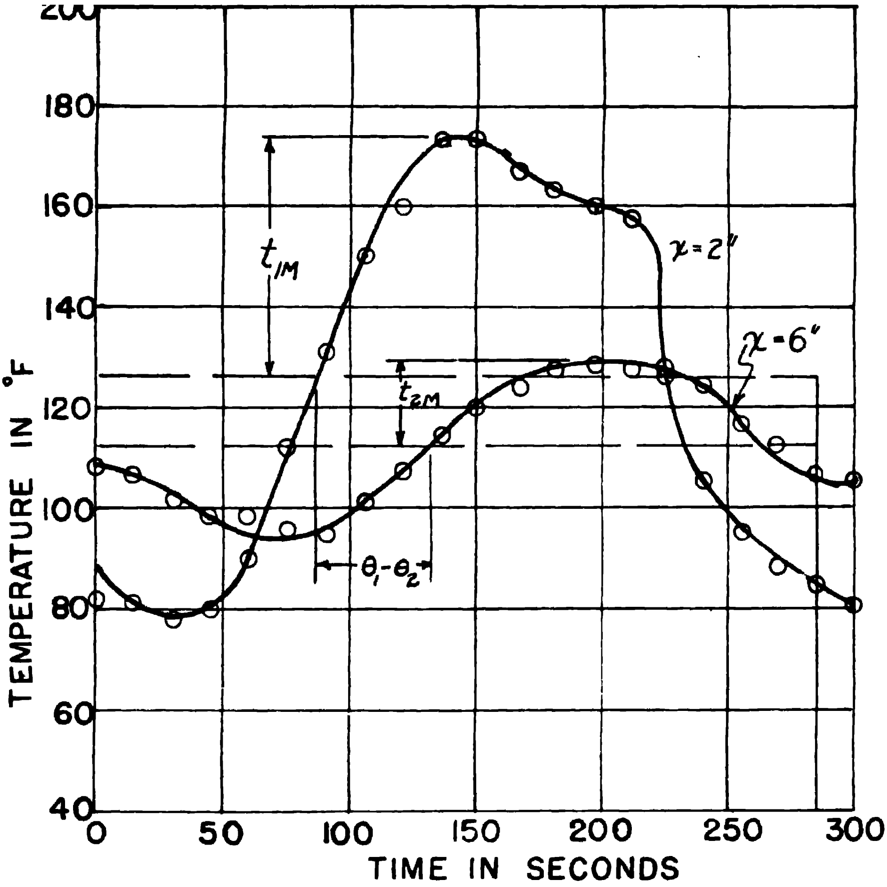
From these two definitions it appears that, since heat must flow to the thermometer from the substance of which the temperature is to be measured, the reading of the thermometer will depend upon the nature of the contact between the thermometer and the substance being tested. The second definition permits the inference that instrument readings are not synonymous with true values.

The pertinent characteristics of temperature include first, its measurable effects and secondly, its variation with time. The measurable effects have been listed in the introduction to this paper and are sufficiently displayed by the scheme of instrumentation there outlined. The variations of temperature with time may be grouped under the following heads:

Temperature fluctuating with small constant amplitude about a mean value;
Temperature changing periodically with time (constant amplitude);
Temperature changing transiently before or after steady periodic or steady mean value states, as listed above.

The machine shown in Fig. 1 is used to demonstrate the first two types of temperature variation listed above, both of which are steady states. The apparatus shown consists of two essential parts: a stationary copper rod ¼″ in diameter by 5 feet long fitted with thermocouples distributed along it, and a motor-driven arrangement for alternately heating and cooling one end of the copper rod. The copper rod is well insulated with 85-per cent magnesia pipe covering to raise its average temperature well above the room temperature. Heating is accomplished by an open gas flame and cooling by a stream of water. The motor pulley is of the step type, so that several different periods may be obtained. Experience has shown that the period of the heat cycle should be from 4 to 8 minutes in length. Such lengths of period permit accurate observation of temperature to be made and also produce observable penetrations of the temperature change into the rod. The rod is made of copper to reduce radial variations of temperature.

In operation the unit is run steadily for a length of time sufficient to obtain steady state conditions as shown by a recording potentiometer. The students then measure temperatures at several points along the rod over periods of two complete cycles of temperature variation. The maximum temperatures at the different points are oriented with respect to time. Typical data obtained by students are shown in Fig. 2. From this figure it is seen that the amplitude of fluctuation decreases as distance from the heated end of the rod increases. The amplitude becomes too small to measure at a distance of 8 inches from the heated end of the rod. The wave shape changes with distance along the rod, becoming more nearly sinusoidal as the distance from the heated end increases. As indicated, the time-lag data are used to compute the thermal diffusivity of the copper rod. The value of diffusivity



$$t = t_{0M} e^{-\sqrt{\frac{\pi}{a\theta_0}}x} \cos\left[\frac{2\pi\theta}{\theta_0} - \sqrt{\frac{\pi}{a\theta_0}}x\right] x \sim \text{ft};\ \theta \sim \text{hr};\ a \sim \frac{\text{ft}^2}{\text{hr}}$$

t = temperature at section x and time θ measured above the mean value at the same x.

Computations:

1. Thermal diffusivity, a

$$a = \frac{\theta_0}{4\pi}\left(\frac{x_1 - x_2}{\theta_1 - \theta_2}\right)^2$$

$\theta_1 - \theta_2$ = time lag between points x_1 and x_2

$$a = \frac{285}{4\pi \times 3600}\left(\frac{.333 \times 3600}{46.2}\right)^2$$

$$= 4.17\,\frac{\text{ft}^2}{\text{hr}}$$

From accepted values $a = \frac{k}{C_{p\gamma}} = 3.99\,\frac{\text{ft}^2}{\text{hr}}$

2. Decrement of amplitude.

t_{1M} max. temperature at x_1

t_{2M} max. temperature at x_2

$$\log_e \frac{t_{1M}}{t_{2M}} = \sqrt{\frac{\pi}{a\theta_0}}\,(x_2 - x_1) =$$

$$\sqrt{\frac{\times 3600}{4.17 \times 285}} \times (.333)$$

$$= 1.02$$

$\therefore \frac{t_{1M}}{t_{2M}} = 2.77$. By test $\frac{t_{1M}}{t_{2M}} = 2.82$

References: Carslaw, "Conduction of Heat," p. 50; Boelter, "Heat Transfer Notes," p. VI-6.

FIG. 2. Periodic temperature variation.

so obtained is used to check the measured amplitudes of temperature variation. Temperatures near the heated end of the rod exemplify the steady state periodic type of variation, while those far from the heated end exemplify the steady state mean value type of variation.

Transient unidirectional variation of temperature is exhibited by means of the device shown in Fig. 3. It consists of a box containing dry sand in which are buried an electric heating element in a glass tube and several thermocouples at known locations. A pan of water is placed on top of the sand to maintain constant surface conditions. The sand is used rather than metal or 85-per cent magnesia because of its low thermal conductviity and its ease of arrangement. The relative dimensions of the box and heater are such that the heat flow near the center of the rod's length closely approximates that for an infinitely long cylindrical source. This experiment requires observations at intervals over a period of several hours. In this case other experiments are performed between readings. Initially the temperature is uniform throughout the sand. The heater is then turned on and the electrical input maintained constant. Temperatures at various points in the sand are measured as a function of time. A typical set of data obtained by students is shown in Fig. 4. It will be seen that the experimental data agree well with the computed values.

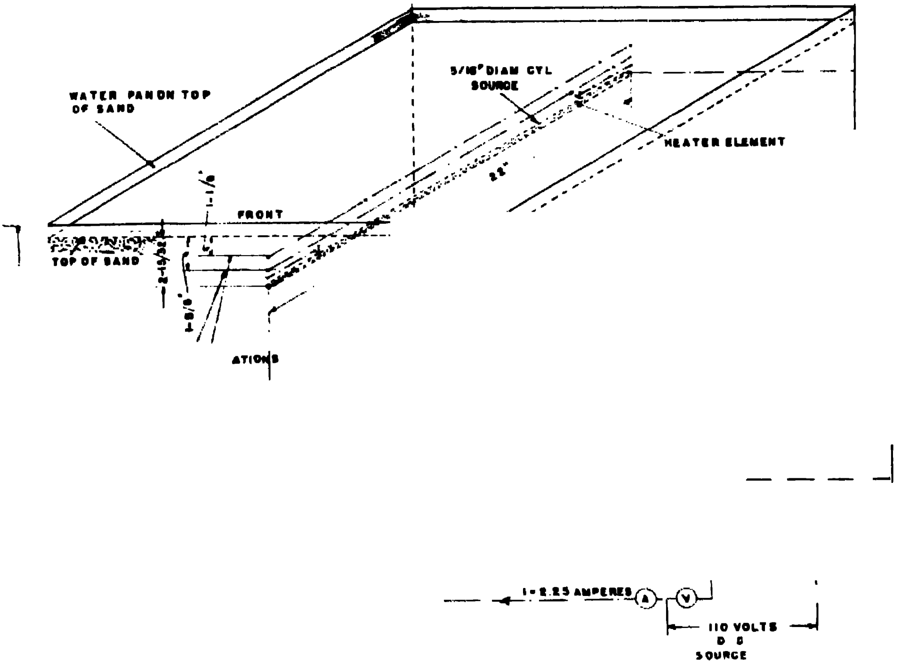
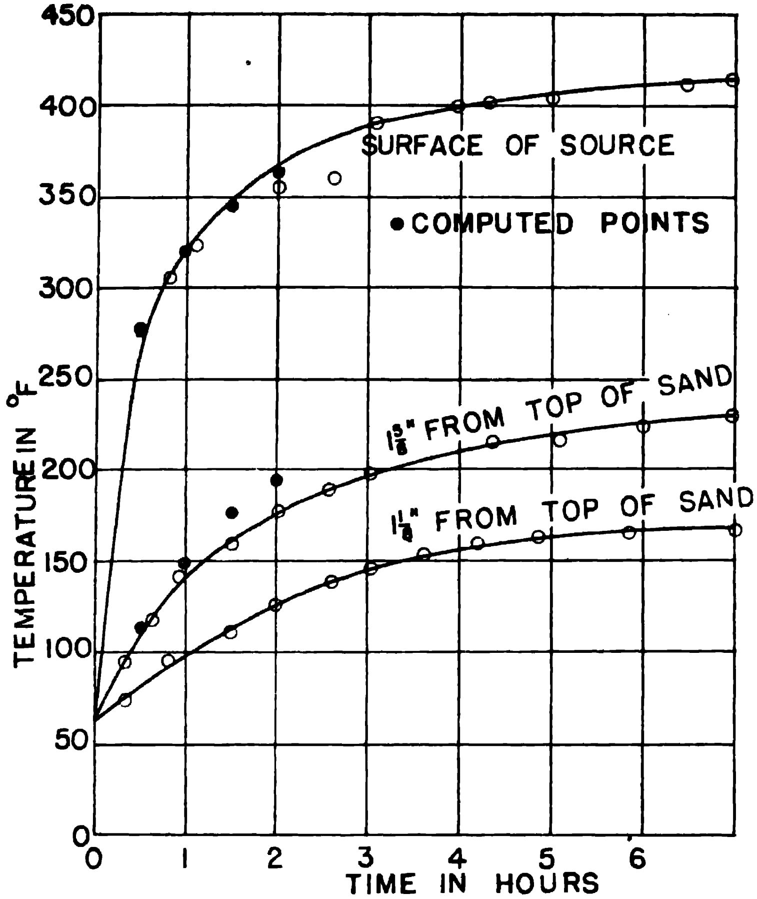


FIG. 3. Device for transient temperatures.

Characteristics of Thermometers and Thermocouples

In the experiments so far conducted it has been assumed that the instruments used were capable of indicating standard values and of following accurately the



$$t = \frac{q}{5.458K} \int_{-\infty}^{\log \frac{a\theta}{r^2}} e^{-}\left\{ \frac{r_0^2 + r^2}{4a(\theta - \theta')} J_0 \right\} \left[\frac{irr_0}{2a(\theta - \theta')} \right] d(\log\{a(\theta - \theta')\})$$

t = temperature rise in time $(\theta - \theta')$ at a radius r from source of radius r_0, $t \sim$ °F, $r \sim$ ft;

K = thermal conductivity $\dfrac{\text{B.t.u.} \times \text{ft}}{\text{ft}^2 \times {}^\circ\text{F} \times \text{hr}}$;

a = thermal diffusivity, $\dfrac{\text{ft}^2}{\text{hr}}$;

q = rate of heat generation per unit length, $\dfrac{\text{B.t.u.}}{\text{ft} \times \text{hr}}$;

J_0 = Bessel's function, first kind, zero order.

This equation may be readily solved by the use of plotted results for particular values of $\dfrac{r}{r_0}$ and $\dfrac{a(\theta - \theta')}{r_0^2}$. For sets of these curves see A. B. Newman, *Ind. Eng. Chem.*, 13, 29 (1931); Boelter, "Heat Transfer Notes," pp. VII-13.

FIG. 4. Transient heat flow from a cylindrical source of constant power.

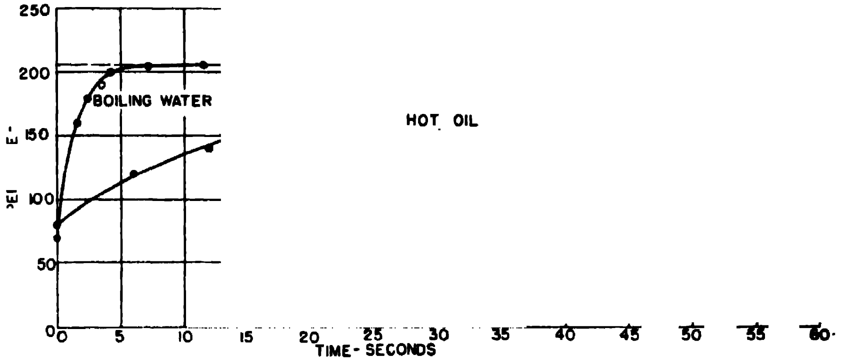


FIG. 5. Time lag of a mercury-in-glass thermometer.

variations of temperature with time, the emphasis having been upon the characteristics of temperature. The student's attention is next directed to the characteristics of the instrument, the two properties investigated being the comparison of indicated values with standard values and the ability of the device to follow temperature variations. The thermometer is first tested for its time response. A water bath is heated over a Bunsen flame to the boiling point. A thermometer with the bulb wetted is then placed in the water and the time measured for its indication to become correct. The thermometer is cooled and then placed in an oil bath at the same temperature as the water bath. The response curves are shown in Fig. 5. Comparison

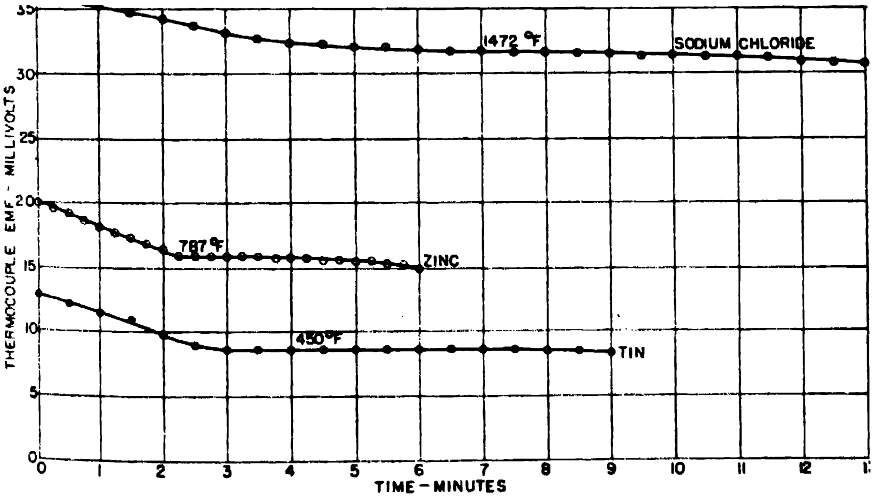


FIG. 6. Calibration of a No. 10 Chromel-Alumel thermocouple.

of the thermocouple with the thermometer is made by first inserting the thermocouple in the water and balancing the potentiometer. The thermocouple is then wetted with cold water and plunged into the hot water. The response of the thermocouple is found to be more rapid than the potentiometer indicator can follow. This

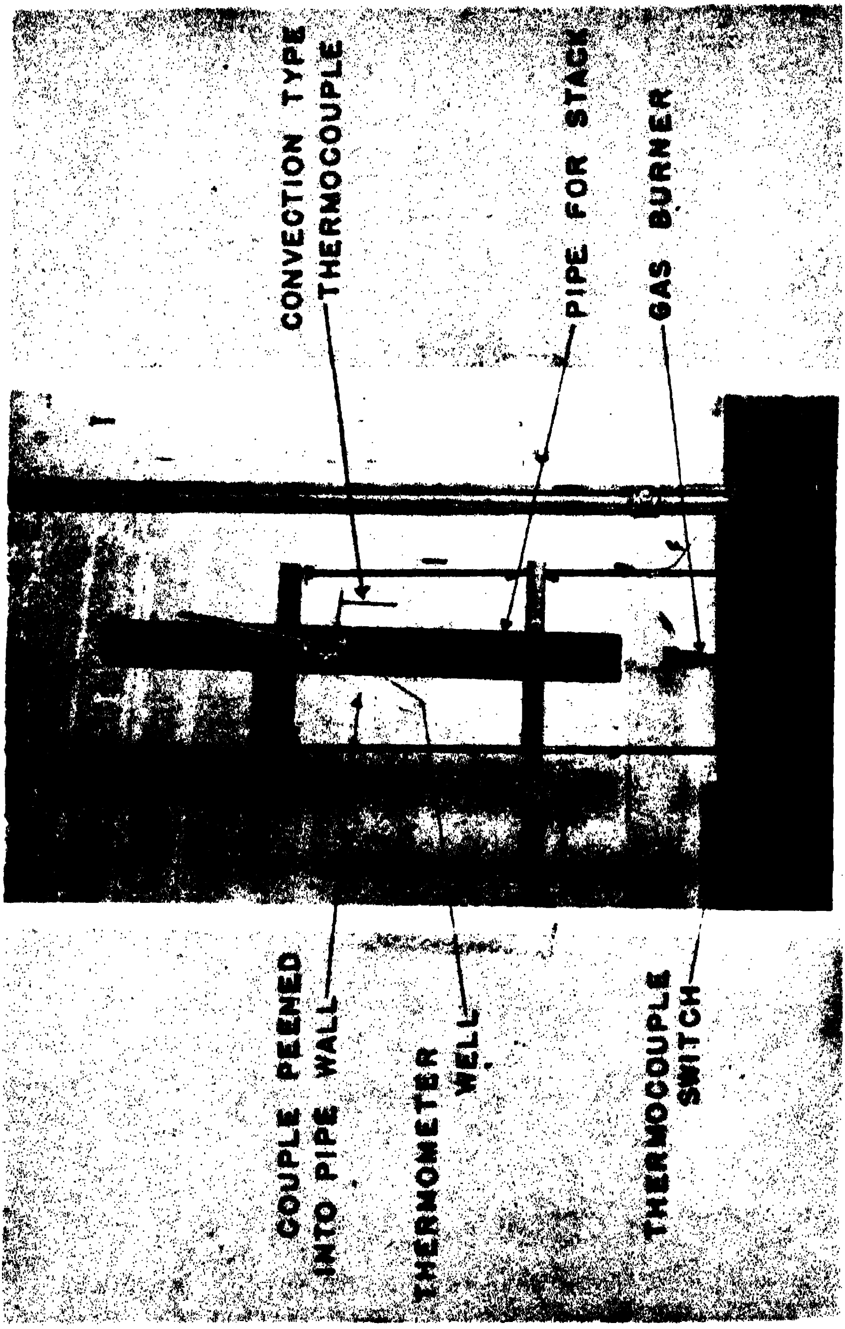

CONVECTION TYPE THERMOCOUPLE
PIPE FOR STACK
GAS BURNER
COUPLE PEENED INTO PIPE WALL
THERMOMETER WELL
THERMOCOUPLE SWITCH

Fig.

mp

demonstration serves to show the great thermal capacity of the thermometer as compared with the thermocouple. The product of the thermal resistance and capacity may be readily calculated.

The calibration of a thermocouple is accomplished by using fixed points. A series of crucibles containing materials having known fusion points is used. Solid materials are heated over a flame to somewhat above the fusion temperature. The thermocouple is then inserted in the bath and slow cooling permitted. Thermocouple voltage is measured at regular intervals and the time-temperature curves shown in Fig. 6 obtained.

Characteristics of the Instrument Station

The attention of the student is next directed toward some of the errors introduced by the necessity for heat interchange between the measuring device and the material for which the temperature is to be determined. The apparatus shown in Fig. 7 is used to demonstrate errors due to heat flow in thermocouples and thermometer wells. In this equipment a black-iron pipe is mounted vertically as a stack for the combustion products of a large gas burner. A thermometer well and three thermocouples are used. One thermocouple is peened into the pipe wall and indicates the temperature of the metal. The second thermocouple is placed in the gas stream with a large bead at the junction exposed to radiant heat interchange with the walls. The third thermocouple is of the convection type, shielded from radiant heat interchange with the walls. The thermometer is placed in a thermometer well, filled with oil. After steady conditions are obtained, a series of readings of each device is taken and the average values computed. For one such test the following values were obtained:

True gas temperature (convection thermocouple)	343 °F.
Pipe wall temperature	192 °F.
Exposed thermocouple temperature	324 °F.
Thermometer well temperature	269 °F.

The errors of the exposed thermocouple and of the thermometer well have been analyzed elsewhere.[3] Applying the results of that analysis to the present case the computed errors of the exposed thermocouple and of the thermometer well are 23 °F and 52 °F respectively. These figures check the measured values reasonably well, establishing the validity of the analysis.

The second experiment in this group demonstrates the determination of surface temperatures with thermocouples. The apparatus consists of a horizontal pipe mounted in a wooden frame and fitted with thermocouples fastened to it in various ways. Heat is generated within the pipe by an electric heating element. Control thermocouples are peened into the pipe to establish a temperature gradient along the pipe. Readings are then made of voltages produced by all couples under steady conditions. Typical comparative temperatures are given below:

Thermocouple peened into hole in rust-covered surface: 492 °F.
Thermocouple peened into hole in brazed-over surface: 465 °F.
Thermocouple brazed on surface: 498 °F.
Thermocouple brazed on surface and wrapped once around pipe: 500 °F.
Thermocouple immersed in oil, filling small hole drilled partially through the pipe: 420 °F.

All these readings were made with No. 24 gage iron-constantan thermocouples. The conclusion from this experiment is that accurate surface temperatures can be obtained only when good thermal contact exists between thermocouple and heated metal, and when the surface is not destroyed by the thermocouple connection.

This completes the list of experiments performed on the subject of temperature measurements at the University of California. The list, while not extensive, does introduce the student to some of the ideas of temperature measurement. After having performed this series of tests it is expected that the student will be familiar with the primary methods of temperature measurement, will be able to distinguish between instrument readings and true values, and will be competent to criticize a given installation of measuring equipments.

Suggestions for Additional Experiments

The Cathode Ray Oscillograph presents interesting possibilities for the study of temperature measurements. With its use the periodic and mean value types of temperature variation could be demonstrated, using higher speeds and lighter apparatus than that described in this paper. It could be used also for determining the time-response curve for a thermocouple.

The equipments and experiments listed obviously do not exhaust the possibilities of the subject. Some of those which have been suggested are:

- Characteristics of temperature
  - Transient temperature variation due to the cooling of a cylinder or flat plate
  - Steady temperatures produced by the condensation of steam or other vapors
- Characteristics of temperature-measuring devices
  - Stem correction of mercury-in-glass thermometers
  - Time lag of vapor-pressure instruments or of resistance thermometers
  - Calibration of optical pyrometers
- Characteristics of the instrument station
  - Temperature gradients along tubes of remote-reading liquid-expansion and vapor-pressure thermometers
  - Difficulties of obtaining correct temperatures for flowing liquids

In addition to the preceding list the thermopile radiometer, described in another paper[4] at this symposium, is sufficiently rugged and sensitive to be used by students for the study of radiation and temperature measurement. Its advantage over other, similar instruments lies in its large current and voltage-producing capacity, which permits measurements to be made with portable instruments.

The Teaching of Mensuration

A separate course has been advocated for the study of mensuration, just as a separate course is at present offered in some colleges for the study of report writing. Since, in the majority of engineering careers, these subjects are auxiliary to the main topic of an investigation, it would seem desirable to introduce them in a similar auxiliary relationship during undergraduate instruction. Furthermore, a certain economy of the student's time and effort results, since the examples illustrating report writing and mensuration form parts of a report otherwise necessary. Experience at the University of California indicates that a satisfactory program of instruction on mensuration may be carried out as part of the already established laboratory courses.

Acknowledgments

The experimental equipment described in this paper has been developed during the past ten years by the laboratory instructional staffs. The writers gratefully acknowledge the contributions of this group as a whole. Special recognition is due to Mr. D. O. Rusk, now employed by the Associated Oil Co., to Mr. C. R.

Dodson, now employed by the Standard Oil Co., and to Dr. V. H. Cherry, recently deceased.

Discussion

C. A. McKeeman, Assistant Professor of Mechanical Engineering: The laboratory instruction of the engineering student in the art of making accurate fundamental measurements is always a problem, especially since the student is usually anxious to progress to the testing of actual machines. Consequently experiments appealing to the student and visualizing for him the difficulties involved in making primary measurements are extremely important. The authors of this paper are to be congratulated on giving the subject "sales appeal."

At Case School of Applied Science it is felt that a separate course in mensuration is not feasible for the mechanical engineering student. His time is already crowded and the provision of ample time for mechanical engineering laboratory itself is a problem. In addition, it is logical that the student take the mensuration phase of the work before entering into the testing of engineering equipment, thereby placing the need for this instruction in the first term of the junior year. At that time the basic principles have not been established with him. Any separate course in mensuration would thus fall in a fifth year of work or, perhaps, in the senior year of a mechanical engineering curriculum not requiring a thesis for graduation. Experience at Case has been that of the authors: namely, that a few weeks of laboratory devoted to mensuration, followed by experiments having adequate instrumentation, gives positive results.

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Progress in Standardization of Letter Symbols for Heat and Thermodynamics

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Let us go over in our imagination the history of a page of a technical publication sprinkled with mathematical equations. The author, who may be a great master, knew his subject (we hope) and had had long familiarity with the letter symbols in the equations for the various concepts. He probably learned these symbols when he was a young college student, and when he used a concept such as enthalpy, the old symbol for it, such as I, instantly appeared in his mind without even a thought. And so he writes equation after equation, never having to pause for an instant to think that intrinsic energy is U, entropy is ϕ, and so on.

Then ordinary people such as you and I get the publication to digest. It is said that the sight of a good meal makes the digestive fluids of our stomach flow, but I am afraid lots of us don't have any flow of pleasure when we look over a page of heavy mathematics. A few of the symbols, such as p for pressure and T for absolute temperature, we readily recognize. We are presumably making reference to a *single section, and have not gone over the whole text.* U, U, *that's velocity, isn't it? We paw over the pages looking* for a table of symbols at the beginning of the book. No, maybe it is at the end. No, maybe it is at the beginning of the chapter, or maybe it is at the end of the chapter. No, there isn't a table of symbols anywhere. We read a couple of pages and find that somewhere in the middle of the text the author says, "Let U be intrinsic energy." And so we struggle along, having to pause at every third or fourth symbol to find out what it means. After a lot of time is spent this way, we start all over again with an equation, knowing pretty well by now what the symbols are, so that we can make a stab at finding out what the equation is all about.

Next, let us visualize the millenium when all technical authors are tame, and every one of them uses exactly the same symbol for each concept. A little past experience has made us familiar with most standard symbols so that when we see H, U, μ, etc., in the equations, we instantly know what the author means without a conscious thought, and can immediately concentrate on trying to understand the equation (which is often tough enough).

This is the situation that the American Standards Association project on Letter Symbols is trying to bring about. We hope to get the lists of symbols so standardized that physicists, mechanical engineers, electrical engineers, chemical engineers, and everybody using a given concept, will use the standard letter symbol familiar to all of us.

Existing diversities make progress in some directions difficult, but a proper spirit of tolerance, and compromises with points of view other than one's own, will give success in the end.

This standardization process is fairly well along at the present time and anyone who writes a paper or report without using the existing standards is going to be punished the next time he tries to get a ⅜ in. bolt as a spare part for his auto, by finding that the only available supply dealer didn't think that the standard number of 16 threads looked beautiful so had only ⅜ in. bolts with 24 threads in stock.

By way of a practical demonstration, one of the sponsors for this ASA project Z10 has made it possible for the Committee in charge of the arrangements for this symposium to present a tentative draft of the proposed revision of the present American Standard on "Letter Symbols for Heat and Thermodynamics Including Heat Flow," to each of the authors presenting papers. This proposed standard represents an attempt to present in a single approved list the letter symbols needed by workers in the subject of "heat" whether they be physicists, engineers, chemists, physical chemists, or specialists on radiation and heat transfer.

This is, however, only one of the eleven subprojects initiated by the Sectional Committee on Letter Symbols and Abbreviation for Science and Engineering (Z10) for which the AAAS, AIEE, ASCE, ASME, and SPEE are joint sponsors under the procedure of the American Standards Association.

On Classifications of Temperature Instruments

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1. Primary Considerations

It is recognized that a reclassification of temperature instruments is both wanted and needed by workers in science and in industry. Actually, there is a diversity of needs or wants among various fields of education, research, industry and "sales engineering." The authors of text books, of articles in periodicals and of commercial bulletins will of course look to this Symposium, but they will continue to make up different lists, as in the past. Hence the need is not for one new classification, stamped "Official," to be slavishly copied. (Even "official" spellings and grammars never win universal acceptance, always suffer mutilations, always undergo alterations.) The practical need is for a series of classifications—as far as possible an integrated and coördinated series—prepared by different workers to satisfy different wants but "written in the same language." In short, diversity without disorder.

This is not a one-man job. In the first place, the revision of terminology making possible a "common language" implies general agreement. In the second place, the rapid development of new instruments, as well as the increasing applications of the newer methods of temperature measurement and control in industries, call for a meeting of representative minds.

Would a meeting of *persons,* around a conference table, bring forth a definitive classification and a definitive terminology? Experience has taught that the result of such a procedure probably could not be definitive. It is only after such conferences have approved final drafts that numerous interested parties are heard from whose existence was unknown or whose interest was unmanifested—but whose influence upsets the applecart.

Being a one-man job, this paper, then, will not attempt to lay down *the* classification or *the* terms, but it will set forth considerations underlying the construction of classifications that can be definitive in framework if not in detail.

Recognizing the necessity for a meeting of minds, it is intended here merely to "open" such a meeting by reporting briefly on the ground already surveyed, and to facilitate the work of persons serving different fields by making available some results of rather tedious researches in methodology, begun in 1924.

2. Ubiquity of Temperature Renders Completeness Impossible

Only a century ago, temperature was one of a scant score of known magnitudes; today it is one of hundreds. But the unique thing about temperature is that it affects the measurement of nearly all of these hundreds of known measurables. Ambient temperatures, conductor temperatures and various local temperatures affect nearly all the thousands of distinct methods of measuring these athermal conditions and properties. Consequently, almost every time a new method is devised for determining a physical or chemical value, the temperature coefficient must be taken into account. "Watch out for the temperature error" is the injunction most often heard wherever any measurement is to be performed in any field of work. Eight years ago a chemist sought advice on a constant-temperature enclosure for an electrolytic conductivity cell because the particular solution she was working with had a notoriously high temperature coefficient of conductivity. Her adviser jokingly suggested that she use a sealed thin-walled tube containing a few cc's of that solution instead of a platinum coil for the measuring element of a resistance thermometer. That was a jest eight years ago. Two years ago the National Bureau of Standards published the use in radio-meteorography of a resistance thermometer with just that kind of liquid-filled measuring element. "The temperature error of today may be a temperature measurement method tomorrow."

3. An Exhaustive Scheme Is Possible

Hopelessly impossible as is the task of writing down an exhaustive list of instruments or even of methods—in thermometry and pyrometry, or in any other field—it is possible to formulate basic schemes, any of which would be exhaustive for all practical purposes. For example, the whole universe can be divided into (1) Abstract and (2) Concrete. The trick of the exhaustiveness here is that it depends on definitions.

In the field of temperature instruments, therefore, it is possible—and relatively easy—to devise a fundamental classification consisting of a collectively exhaustive list of categories. Examples:

1. "Scientific"
2. "Industrial"
3. "Domestic"
4. "Universal"

(B)

1. "Laboratory"
2. "Plant"
3. "Field"
4. "Universal"

(C)

1. Contact
2. Distance

(D)

1. Local
2. Telemetering

(E)

1. Indicating
2. Maximum- or minimum-registering
3. Recording
4. Controlling
5. Combination

(F)

1. Portable
2. Board- or wall-mounted
3. Built-in
4. Convertible

(G)

1. Single-point
2. Selector-switch type

(H)

1. "Ready-to-use" or "factory calibrated"
2. Requires calibration

And so on, perhaps, beyond (Z). It will be found more and more difficult, however, to achieve exhaustiveness without "cheating" by including a final catch-all named "Miscellaneous."

4. Avoid Dependence on Undefined Terms

Consider now the actual use of a scheme of classification. A busy engineer or chemist, desiring a readable dial to be placed conveniently, while the primary element of the system has to be placed in an invisible location, would be most interested—at that particular moment—in classification (C): (1) Contact; (2) Distance. He would ring up a supply house and order their "Model 30220 *Distance Type*" with ten-foot capillary, and it would make little difference to him that the primary element (say a mercury-filled steel bulb) was in physical contact with the substance whose temperature he desired to measure. To all physicists and to most technicians, however, a mercurial system would belong in the "contact" category and "distance" would mean an instrument with a measuring element located at a distance from the body whose temperature is to be measured. Obviously, then, scheme (C), though it has been adopted as the basic scheme of some industrial classifications, could not be accepted universally unless a recognized authority defined the terms "contact" and "distance."

A similar defect characterizes other examples, particularly (A), which suffers from acute "user-itis": a vest-pocket thermometer would belong under 1, 2, 3 or 4 according to the occupation pursued by the wearer of the vest.

Scheme (B) suffers from a different disease which we might call "usage-itis": it depends too much on the meanings which a reader attaches to the names of its four fundamental categories.

On the other hand, most of the names of the categories in examples (E), (F), (G) and (H) are "tight definitions"—for purposes of classification, at least. A particular thermometer will usually[*] belong in one category, and in only one.

This brings us to the second law of methodology: the categories of a "perfect" classification should be *mutually-exclusive*. This requirement is extremely difficult to satisfy in devising general-purpose or "popular" classifications in any branch of science or engineering, for two obvious reasons: (1) the commonest current terms are nearly always the loosest; (2) newly-coined terms become ambiguous when they pass into the vernacular.[†]

However, by an old methodological trick, it is easy to satisfy this requirement of mutually exclusive categories (as well as the first: collectively exhaustive categories.) The "perfect" general-purpose classifications of *things* are those made up of quantitatively graded categories defined by arbitrary intervals. Examples:

(I)

1. Limits of practicable ranges extend from 0 °Abs. to 100 °Abs.
2, 3, 4, etc. Similarly defined.

(J)

1. \$4.99 or less
2. \$5.00 to \$99.99
3. \$100 to \$499.99
4. \$500 or more

Such classifications find logical uses as supplemental references.

Many other illustrative notes on methodology could be added, but this dry subject may be concluded briefly (and dogmatically) with three broad rules governing the classification of *things:*

(1) The narrower the scope of interest, the easier it is to meet the two principal requirements. See examples (C) to (J).

(2) The fewer the prime divisions, the easier. Hence, the easiest scheme is a simple "either-or" bifurcation, like "abstract and concrete," "live and dead," "subjective and objective"—or like examples (C), (D), (G) and (H).

(3) Within each prime division, likewise, the easiest scheme is a simple "either-or."

Applying these rules may not lead to perfection but it offers a choice of schemes at each stage. Here is the beginning of one possible classification:

(K)

"Divisions"	*"Classes"*	*"Types"*	*"Sub-types"*	*"Varieties"*
1. Thermometers	1. Mechanical 2. Electrical	1. Expansion 2. Pressure	1. Fluids 2. Solids	1. Liquids 2. Gases
2. Pyrometers	1. Radiation 2. Optical			

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[*] Usually, but not always: The cooling-water thermometer of an automobile, for example, is both "built-in" and "board mounted."

[†] And even when they don't. Consider what happened to "kata-thermometer" since Dr. Heberden coined it a hundred years ago to signify one *variety*. It now signifies half a dozen *types* of instruments!

This particular example, of course, is an extreme example of dependence on definitions. In the first place, it is based on the assumption that the definitions of "thermometer" and "pyrometer" already coincide exactly with the prime division of all temperature instruments into "contact" and "distance." (Definitions much tighter than prevalent usage.) In the second place its exhaustiveness depends on assigning to the "electrical" class most instruments utilizing non-electrical effects, simply because it is possible to measure anything electrically.* (Definition much looser than prevalent usage.)

5. An Obvious Solution: Incomplete Special-purpose Classifications

Let us consider the basic classifications, if any, now in vogue.

At present we have a glorious monument to the genius of our predecessors. Unfortunately, the monument is awry. It is a list containing some obsolete terms: most nouns fairly usable but most adjectives vague. Its fundamental division (Thermometry and Pyrometry or Thermometers and Pyrometers) is no foundation and never was. Any such dividing line must be arbitrary. The monument's architecture is hybrid: old classifications are jumbles of rational lists of principles all mixed up with unsystematic lists of forms, vague lists of vague ranges and other illogical lists.

Table 1. "Industrial" Classification of Temperature Instruments

I. "Thermometers"

Liquid-in-glass (Visible-column).
- a. Mercury—customary types.
  - (1) Industrial (complete protection)
  - (2) Semi-industrial (incl. special-purpose)
  - (3) Miscellaneous (pocket, wall, etc.)
  - (4) Etched-stem ("laboratory," "testing")
  - (5) Enclosed-scale
- b. Mercury—Beckmann type.
- c. Mercury—special glass.
- d. Alcohol.
- e. Toluol.
- f. Pentane.
- g. Gallium in quartz.

2. *Solid expansion.*
- a. Metal and refractory.
- b. "Two-metal" (rod, tube, etc.).
- c. "Bimetal" (deflecting strip).

3. *Pressure-spring.*
- a. Mercury.
- b. "Xylene."
- c. Vapor-pressure.
- d. Gas.

4. *Electrical Resistance.*
- a. Platinum.
- b. Nickel, etc.

5. *Thermoelectric.*
- a. Rare-metals.
- b. Special alloys.
- c. C-SiC.

II. "Pyrometers"

Total-radiation.
- a. "Hand."
- b. Autometric, autographic, etc.

2. *Selective-radiation.*
- a. Visual.
  - (1) Brightness matching.
  - (2) Color matching.
- b. Autometric, autographic, etc.

3. *Fusion.*

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* And on other such assignments. For example, pyrometric cones would come under expansion of solids by stretching "expansion" to mean *all* dimensional changes, including deformation without change of volume.

At present, then, each worker, from the science teacher to the sales-manual writer, faces a dilemma: respect for conventions and usages, *versus* what he knows to be the requirements of a "good job" even if he never heard the word methodology. He therefore assembles the data of greatest interest to his audience, arranges them in a convenient way, gratefully uses the available single-word designations, tries to define other classes and types in the fewest number of words without departing too far or too often from usages, puts down one weighted average for each numerical datum . . . and calls it a day. In some cases, timeliness (or pure luck) makes a special-purpose tabulation more widely useful than originally intended. Table 1 is a revision of an "industrial classification" first published in 1928: though still far from complete, it is believed to represent a useful compromise.

6. Suggestions for Future Work

The preceding sections of this paper are the impersonal "minutes" presented at the opening of the meeting of representative minds. Now, under the head of new business, miscellaneous reports, remarks and motions will be submitted by one individual worker (who represents only himself but makes bold to speak for a segment of the field of vocational education, namely, the training of industrial instrument engineers).

Fundamental Definitions. Since the entire area of the subject under discussion is defined by the meanings attached to the words "temperature" and "instruments," it may not be amiss to start with these two words.

Future workers will no longer find any disconcerting elasticity in definitions of the temperature concept, of the absolute scale of temperature and of various temperatures, for these are clarified once for all in other papers and in appendices to be included in the book resulting from this Symposium.

Unfortunately, the word "instrument" pertains to so many fields outside science and industry, and has been endowed with so many different and overlapping meanings, that the meeting of scientific and industrial minds is perplexed by a bewildering embarrassment of riches. The task facing the workers is not so much one of definition as of successive approximations, selections and rejections. First, there is little or no doubt that none but *measuring* instruments should be considered. (This would not exclude automatic controllers: "before a condition can be controlled it must be measured" and "there's a thermometer or pyrometer in every temperature controller.")

A second narrowing down might result, for example, if someone proposed to exclude all devices which utilize irreversible phenomena. Or the consensus would be to recognize all such devices—existing and yet unconceived—but relegate them to a "miscellaneous" category at the end of future exhaustive classifications.

Next, a series of decisions will have to be made as to inclusion or exclusion of certain types of instruments and apparatus not provided with continuous scales. Examples:

(1) Simple fixed-point indicators—from the purest samples of elements or most carefully prepared mixtures, to the cheapest "thermometric" paints and inks—from those used once only and discarded, to those exhibiting reversible changes without fatigue drift. Are they instruments at all?

(2) Devices the "scales" of which are inherently and inevitably discontinuous by reason of their construction as *sets* of the discrete objects referred to in the preceding paragraph. Numerous such devices have been invented.

Not only do differences of opinion tend to clarify the subject but they lead to classifications of the "accepted" instruments on the bases of the discussed topics. Examples:

(L)

1. Continuous scale—the usual form
2. Discontinuous scale consisting of a series of units

(M)

1. Measures once and is discarded
2. Measures intermittently (max. & min., etc.)
3. Measures continuously

Classify by Methods, Not by Things. A fundamental classification might better be based on the essence—on the thing-in-itself rather than on its attributes, because an attribute (such as "portability") may be shared in common by essentially different instruments. Since an instrument is a physical embodiment of a method, a fundamental classification according to classes of fundamental measurement methods may be said to be "ideal" in the same sense that the Carnot-Kelvin working substance and the Kirchhoff blackbody are "ideal."

Since a method of measuring temperature is a method of utilizing an effect of temperature, a classification according to fundamental categories of ***utilized effects*** suggests itself.

Such a classification is here attempted for the first time. For its prime division into a conveniently small number of collectively exhaustive and mutually exclusive categories, we may start from a consideration of the fact that the whole practice of temperature measurement is founded on fixed points. It always is because of a *discontinuous* effect of heating or cooling a substance when it undergoes a change of state that this substance has temperatures of equilibrium. Such effects are always *reversible;* and the combination makes possible the use of these fixed points. Therefore the basic methods defining the international standard are those which utilize *discontinuous reversible* effects. The great majority of methods used in practice, of course, are based on *continuous reversible* effects. A pyrometric cone is an example of a *discontinuous irreversible* effect. These considerations lead to the following prime division:

(N)

I. Methods utilizing discontinuous reversible effects.
II. Methods employing continuous effects.
III. Methods utilizing irreversible effects.
IV. Combination methods.
V. Miscellaneous methods.

These five* mutually exclusive and collectively exhaustive categories may be called "Divisions." Each division except the "miscellaneous" should comprise a list of mutually exclusively and collectively exhaustive "Classes." Each class would be divided into mutually exclusive "Types," collectively exhaustive as far as possible. Within each type, the "Varieties" or Sub-types" may be mere lists.

At each successive stage there is a choice of classification schemes; and opinions will differ. The breakdown of Divisions I, III and IV into perfect classes may not arouse wide interest, but Division II surely challenges the ingenuity of all future workers. To them, therefore, an "industrial" worker who does not pretend to be a physicist leaves the task of elaborating example (N) in a more scientific manner than Table 2, which merely illustrates in part an application of the above-described principles. To comply with space limitations and to save eye-strain by avoiding a profusion of footnotes, Table 2 is left incomplete, but it includes suggestions for alternative subdivisions at various stages. Perhaps its most glaring

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* If, as the writer hopes, the fifth is unnecessary, the classification would be that rarity: one of general usefulness, yet "perfect."

Table 2. Classification of Temperature Measurement Methods.

I. Methods Utilizing Discontinuous Reversible Effects

1. *Freezing point.*
2. *Boiling point.*
3. *Molecular transformation point.*
4. *Solubility.*
5. *Color.*

Etc.

A line must be drawn (both meanings) between equilibrium temperature effects which include the International Standards, and all others.

II. Methods Employing Continuous Effects

1. *Properties of bodies.*

    Thermal expansion, expansivity, expansibility.

    (1) of gases
    (2) of liquids
    (3) of solids

    Instruments are classified by utilized coefficient (linear, cubical); also as cathetometric, extensometric, volumetric, etc.

    b. Conductivity, resistivity (electrical).

    (1) of metals, of alloys.
    (2) of other solids.
    (3) of electrolytes.
    (4) of ionized gases, etc.

    Resistance measurement methods classifiable by type of circuit, by type of instrument (deflection, self-balancing, etc.) and in other ways.

    c. Viscosity, fluidity.
    d. Refractivity.
    e. Vapor pressure.
    f. Magnetic susceptibility.
    g. Sound velocity.
    h. Dielectric "constant."
    i. Elasticity.
    j. Rotatory polarization.
    k. Color of transmitted light.
    l. Color of reflected light.
    m. Hydrogen-ion concentration.
    n. Specific heat.
    o. Compressibility.
    Etc., etc., etc.

2. *Effects between bodies.*

    a. Simple differences of properties.
    (1) Expansivities.
    (a) Bimetallic.
    Etc.

    b. Effects at interfaces ("junctions," etc.).
    (1) Solid vs. solid.
    (2) Solid vs. liquid.
    (3) Liquid vs. liquid.

    Instruments classified also by utilization of effects, modes of conversion of energy: thermoelectricity, etc.

    c. Radiation effects.
    (1) Methods utilizing Stefan-Boltzmann fourth-power law.
    (2) Methods utilizing displacement of maximum energy density. (Color temperatures, of stars, etc.)
    (3) Methods utilizing selected band or effective wave-length.
    (a) Measurement of the monochromatic energy by visual matching.
    (b) Measurement by "extinction" methods, etc. etc.
    (c) Combinations of (a) and (b).
    (a) Selection by filtration as in use of red glass.
    (b) Selection by spectral curve of receiver: photocell, plate emulsion, etc.
    (4) Methods utilizing ratio of energy at two effective wave-lengths. ("Two-color pyrometry.") (a), (b), etc.: Further subdivision into visual and autometric; then by types of electrical ratio instruments, etc.
    (5) Spectroscopic, spectrographic or spectrometric methods.
    Etc.

III. Methods Utilizing Irreversible Effects

1. *Fusion.* 2. *Color change.* Etc.

IV. Combination Methods

1. Methods using a temperature coefficient of an entire assembly. Examples: temperature coefficient of conductance of a thyratron; temperature coefficient of capacitance of a capacitor; temp. coeff. of rate of a clock; t.c. of pitch of almost any musical instr.
2. "Calorimetric pyrometers," "aspiration pyrometers" and other devices requiring transport or transfer or manipulation of the body or of a continuous sample.
3. Methods requiring the introduction of an "indicator" as in line-reversal method.

V. Miscellaneous Methods

(Miscellaneous in the sense of not includable in other divisions.)

defect is that Class 1 of Division II is not even classified: instead of the mere list of fifteen properties (out of 50-odd utilizable) there might be:

a. Mechanical
b. Electrostatic
c. Electrodynamic
d. Magnetic
e. Chemical
f. Electrochemical
g. Optical
h. Magneto-optic
etc.

But many workers will want to make *this* (mechanical, etc.) the first breakdown of Division **II** into Classes, not merely of Class 1 into Types. An argument for this view is that the thermoelectric effect is not mentioned by name. But it is not overlooked: although thermoelectric *power* is a property of a body, this property is not utilized *per se* in temperature measurement and hence is purposely omitted from **II**, 1. What is utilized in thermoelectric instruments is an effect between bodies (**II**, *2*) and specifically an interface effect (**II**, *2*, b).

Workers who agree on the proposition "classify by methods, not by things" might not agree on classifying by utilized effects, or might want to start with a different prime division and allocate the utilized effects in the subsequent stages. As always, there are different possibilities, each of service to some field of science or technology. Here are three more possible fundamental classifications of fundamental measurement methods:

(O)	(P)	(Q)
1. Null	1. Positive	1. Direct
2. Deflection	2. Inferential	2. Indirect

Each pair of terms has been defined by scientific and engineering organizations, for their respective fields. These definitions could be adapted to take care of methods of measuring temperature. Space limitations prevent a discussion. Suffice it to assert that there are pitfalls and to point out, anent scheme (O), that the disappearing-filament method, for example, involves matching brightnesses, not temperatures. Moreover, not all matching methods are null methods. The null method consists in balancing one magnitude against another magnitude of like kind and *opposite direction*, with nothing in between except the null indicator, which only plays the bystander role of a pointer.

Usefulness of Supplemental Classifications. Most of the modern temperature instruments, especially the recorders and controllers, are complicated. Most of them, however, are assemblies of standardized mechanical parts. Standardization and interchangeability provide opportunities for fascinating studies. On a single control board, for instance, one may find five modern electrical self-balancing temperature recorders which look alike (if one does not read the printing on the charts and name-plates) and whose primary elements are: a total-radiation receiver, a resistance coil, a blocking-layer photocell, a photoemissive tube, a thermocouple. A fundamental classification will of course assign them to five different categories according to their different primary elements. But it would be the height of impractical ivory-tower dialectic to refuse to recognize that the five panel-board instruments all belong to one distinct class of electro-mechanical instruments on the ground that these "final elements" are standardized machines which may be hooked up to temperature-measuring elements (as in the five examples just cited) or to elements for measuring pH or plasticity or power or position or pressure or porosity or what not. Not only are such schemes as (D) and (E) useful as criteria, but they may well be carried out in order to analyze and intercompare the various interesting recorders and controllers (and recorder-controllers) which make possible the modern processes of chemical, metallurgical and other industries. Of greatest interest are the "relay type" instruments wherein a feeble measuring system *commands* the operation of power-driven mechanisms. There are no fewer than seven different classes * of relays for this purpose, and hundreds of varieties . . . but this mere mention must suffice.

In fine, the study of modern temperature instruments may start from the beginning or from the end of the indicating, recording, telemetering and automatic-control systems; and both fundamental and supplemental classifications can be multiplied *ad infinitum.*

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* Pneumatic, hydraulic, mechanical, electrical, h-f., electronic, photoelectric.

Chapter 4

Natural Sciences

Temperature Distribution, Extremes, and Trend Tendencies Over the Earth's Surface

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Temperature Distribution

The general distribution of temperature over the earth's surface depends primarily upon the intensity and variation of insolation, modified by marine, continental, desert, and mountain influences. From many considerations temperature is the most important climatic element. Not only does it control the distribution of life on the earth, but most of the other climatic elements, wind, cloudiness, rainfall, etc., are dependent, directly or indirectly, upon the temperature. The world receives practically all its heat from the sun. Very small amounts come from the interior of the earth and from the stars, but these may be disregarded in considering the source of the earth's heat. The sun, with a volume a million times greater than the earth, has a temperature on its surface estimated at 10,000 °F, and probably 50,000,000 °F at its center. Human imagination is incapable of conceiving such conditions. The earth, in revolving around the sun at distances varying from around 91,000,000 miles to 94,500,000, intercepts only a minute fraction of the solar radiation (about 1/2,000,000,000 of it), but upon this small fraction depends all life on the earth.

The air is heated only slightly by the direct passage of the sun's rays through it, so that its temperature depends chiefly upon conduction from the surface on which it rests, to the lower strata near the surface and by turbulence, or convection, to the strata above. The intensity and amount of insolation received at any place on the surface depend upon the angle of incidence of the sun's rays and the length of the day, both of which, in turn, depend upon the latitude. This distribution of insolation accounts for the broader aspects of temperature distribution over the earth, such as the decrease with latitude, the double maximum and minimum near the equator, the seasonal contrasts in middle and high latitudes, etc. However, temperatures often do not conform closely to the distribution of insolation; and the regular distribution of solar climate between the equator and poles which would exist on a homogeneous earth is very much modified by the unequal distribution of land and water, altitude, air and ocean currents, etc. The result is known as physical climate.

Physical climate may be subdivided into three broad classes, marine, continental, and mountain. Marine climate is characterized by conservation in temperature conditions, with relatively small diurnal and annual ranges. The slow changes in temperature of ocean waters result in a retardation of the time of occurrence of maxima and minima, with consequent cold springs and warm autumns.

In contrast, continental climate is severe. In general, the diurnal and annual ranges increase with increasing distances inland. The contrast is emphasized by the difference in the annual range of temperature at San Francisco, California, and Dodge City, Kansas, which are in approximately the same latitude. The annual range (difference between the mean temperature for the coldest and warmest months) at San Francisco is 11.0 °F, and at Dodge City 49.4 °F. Moreover, while the warmest month at Dodge City is July, the maximum temperature at San Francisco is retarded to October by reason of the marine influence. An extreme type of continental climate is found in deserts. Many geologic phenomena and physiographic aspects of the landscape are related to the peculiar condition of desert climates, such as the splitting and breaking of rocks by the extreme diurnal range of temperature, wind erosion, etc.

Mountains influence the distribution of temperature very similarly in all latitudes. The characteristic of mountain climates is a decrease in temperature with increase of altitude, varying greatly under different conditions of topography, but broadly averaging about 1 °F in temperature for 300 feet increase in elevation. The decrease is especially rapid in summer, but under certain conditions may not exist at all in winter because of the phenomenon of air drainage down the mountain slopes into the valleys. Thus the diurnal and annual ranges of temperature on mountains are lessened.

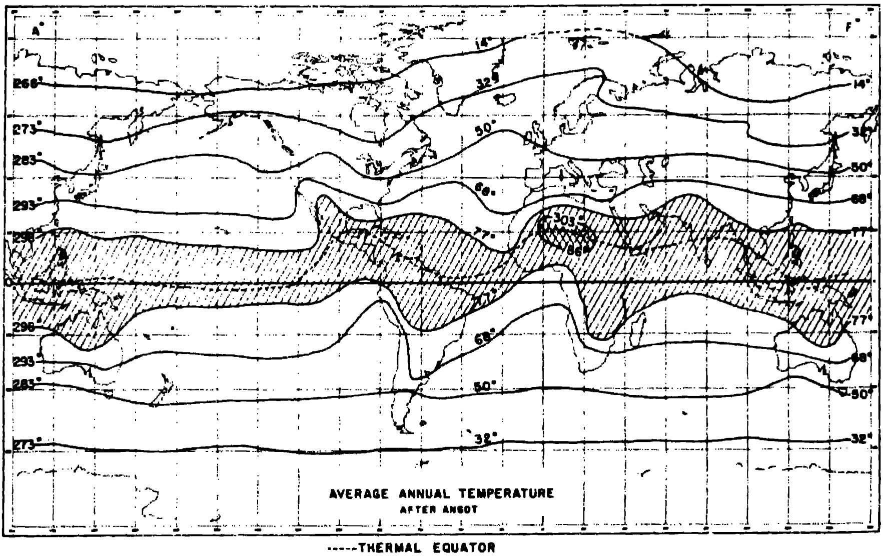
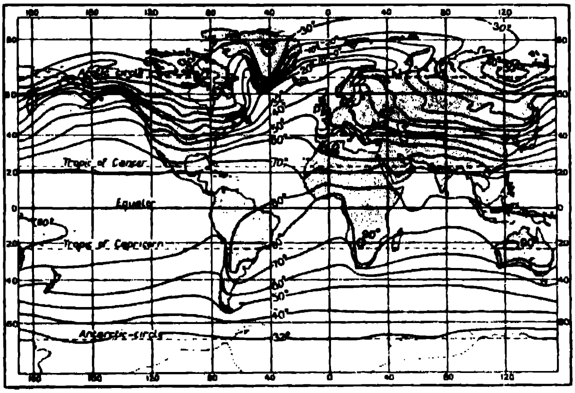


Fig. 1.

Notwithstanding these physical modifications of solar climate, broad, general, latitudinal, delineations of the distribution of temperature over the earth may be made. The mean annual temperature is most significant in the equatorial zone where both the seasonal and diurnal variations are small; but in middle and higher latitudes, with increasing seasonal divergencies, the annual data become progressively less satisfactory as an indicator of actual prevailing conditions. Here annual charts should be supplemented by others showing the extreme (the means for the coldest and warmest months of the year).

Fig. 1 shows that in the equatorial region there is a maximum thermal belt, varying in width, but covering on the average about 25 degrees of latitude, having a mean annual temperature in excess of 77 °F. This belt is disposed in general slightly north of the planetary equator. From longitude 120 E. westward to 120 W. the thermal equator lies on the average about 25 degrees north of the geographic equator; but outside these points the two coincide closely. Poleward from the thermal equator (both north and south), there is a progressive, but irregular, decrease in mean annual temperature to 32 °F at about latitude 60°. Thus, the gradient averages, roughly, one degree in temperature for each degree of latitude.

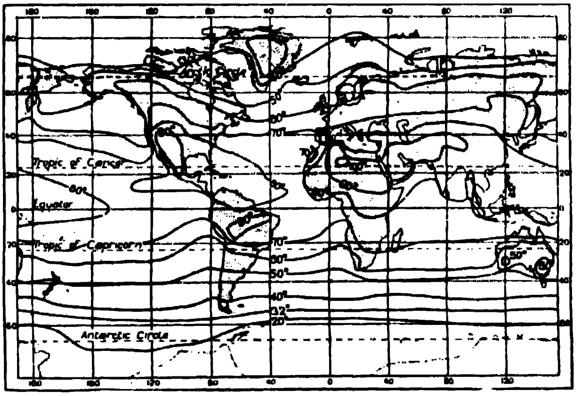


Mean Temperature, January

FIG. 2.

Winter Temperatures

Fig. 2 (Mean January temperature) shows that in midwinter the maximum thermal belt lies well south of the planetary equator, culminating locally in the vicinity of the Tropic of Capricorn, in South Africa and northwestern Australia, with a mean January temperature exceeding 90 °F. In the Northern Hemisphere there are two outstanding winter cold poles, over northeastern Siberia and the interior of Greenland, with January means of −50 and −40 °F, respectively.



Mean Temperature, July

FIG. 3.

Summer Temperatures

Fig. 3 (Mean July temperatures) shows that in midsummer the maximum thermal belt lies well north of the planetary equator, culminating in a mean monthly

July temperature in excess of 100 °F in the vicinity of the Tropic of Cancer in northern Africa. In the absence of extensive land areas and in contrast to the Northern Hemisphere, the Southern Hemisphere has no marked winter cold pole outside the polar region.

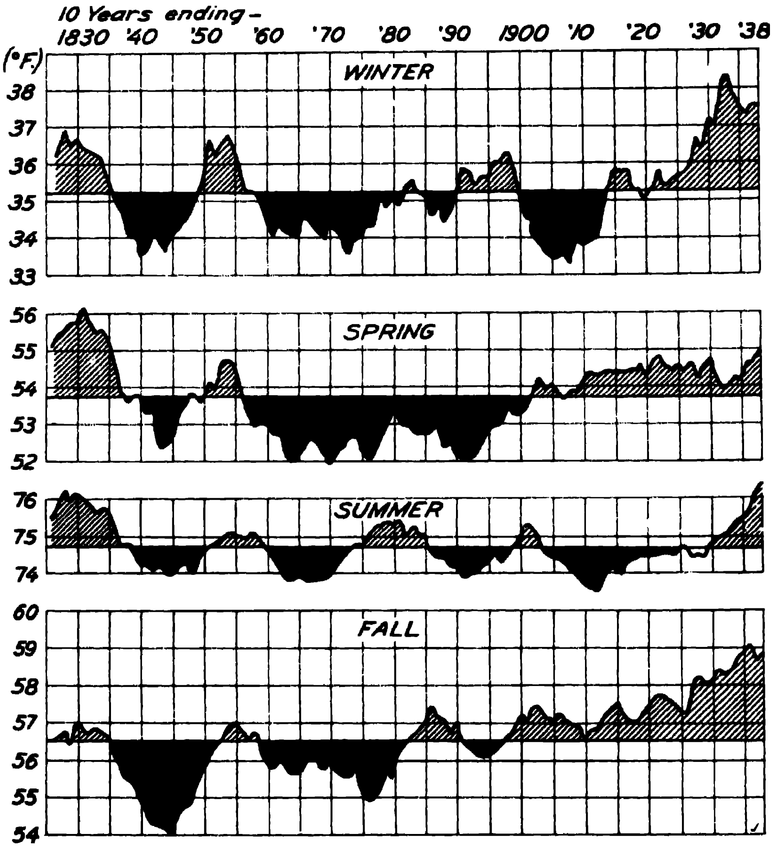


FIG. 4.

Some Extremes of Temperature

The following are some records of extreme temperatures, obtained under standard conditions of exposure, and expressed in the Fahrenheit scale:

Lowest temperature of record, −90.4°, at Verkhoyansk, Siberia. (A minimum thermometer, left for 19 years near the top of Mt. McKinley, Alaska, not in an instrument shelter, when recovered indicated a minimum temperature of approximately −100°.)

Lowest mean temperature for one month, −63.9°, at Verkhoyansk.

Lowest temperature in the United States, −66°, at Riverside Ranger Station, Yellowstone Park, February 9, 1933.

Lowest mean for one month in the United States, −13°, at St. Vincent, Minnesota.

Lowest temperature in Alaska, −76°, at Tanana, in 1886.

Lowest mean for one month in Yukon Territory, Canada, −51.3°, at Dawson, December, 1917.

Lowest temperature in Yukon Territory, −80°.

Highest temperature of record, 136°, in Tripoli.

Highest temperature in the United States, 134°, in Death Valley, California.

Highest mean for one day in the United States, 108.6°, Death Valley.

Highest normal annual temperature in the United States, 76.8°, Key West, Florida.

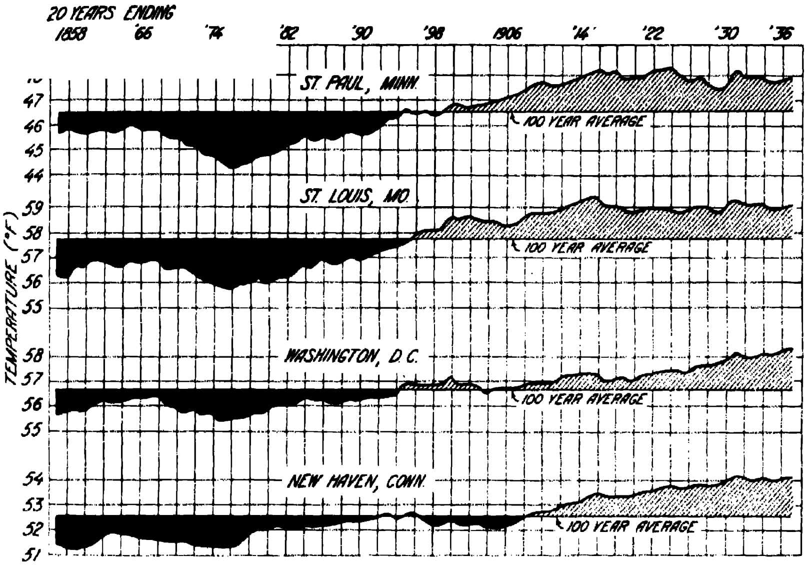


FIG. 5. Twenty-year moving averages of fall temperature.

Temperature Trends

Since the turn of the century there has been such a widespread and persistent tendency toward warmer weather, and especially to milder winters, as to attract considerable public interest; so much so that frequently the question is asked "Is our climate changing?" Historic climate has always been considered by meteorologists and climatologists to be a rather stable thing, in marked contrast to geologic climate and to weather. We know there have been major changes in geologic climate and that weather, which is the meteorological condition at any particular time or for a short period of time, such as a day or a month, is far from stable. Different kinds of weather come and go in comparatively brief alternating spurts, as it were, in short periods of irregular length. However, the phase of weather or climate that has attracted attention is not these short period changes from warm to cool and vice versa, for they are always present, but rather an apparent long-time change to decidedly higher temperatures. Accumulated evidence of many weather records scattered throughout the world indicates that this long-time trend is so outstanding as to require revision of the orthodox conception of the stability of climate.

Climate presupposes the existence of records of sufficient length to indicate the

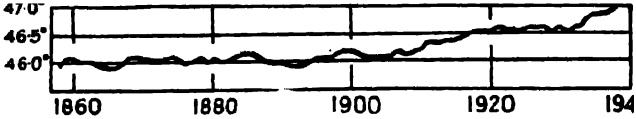


FIG. 6.

"general run" of weather, and consequently the value of a record for such purpose increases with the length of time it represents. Therefore, a record covering only a few years has little value in temperature-trend studies. A recent study of the longer temperature records in different parts of the world shows that the matter of long-time tendency or trend is one of the most, if not the most, important aspect of climate.

Examples of the abnormal warmth that has been in evidence during the last two decades may be cited: Portland, Oregon: 17 of the 20 years warmer than normal; warmest year of record, 1921; every year since 1922 above normal. Omaha, Nebraska: 15 warmer than normal; warmest of record, 1931. Washington, D. C.: 17 warmer than normal; warmest of record, 1921; every year above normal since 1926. Capetown, South Africa: 19 years warmer than normal; warmest of record, 1927. Additional evidence is provided by the lengthening of the summer season and the shortening of the winter. For example, the crop-growing season, represented by the average number of days between the last killing frost in spring and the first in fall, in the vicinity of Washington, D. C., for the 20 years ending with 1906 was 188 days, and for a similar period ending with 1938 it was 206 days. Thus, there has been an increase in the length of the growing season amounting to 18 days. This has great agricultural significance. On the other hand, the winter season, except * 1917-18 and 1935-36, considering the United States as a whole, has been rather uniformly warmer than normal for the past quarter of a century, and, on an annual basis, every year of the last decade had above normal temperature.

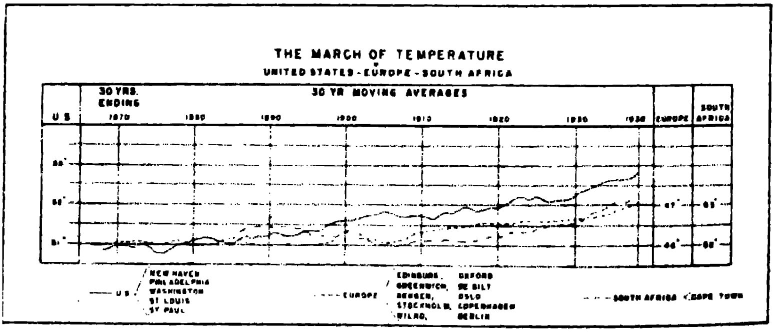


FIG. 7.

Temperature trends for the several seasons of the year have not been uniformly in agreement among themselves. However, Fig. 4, containing data for Washington, D. C., indicates that about a century ago the trend for all seasons was to

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* At this writing, the data for the winter 1939-1940 are not complete, but it is highly probable that this year will also be an exception.

above normal temperature, and rather uniformly below normal in the 60-70's of the last century. For the last quarter of a century in all seasons the data show just as marked abnormal warmth as subnormal some 60 to 70 years ago.

For long-time trend tendencies the fall season (September-November) is outstanding, as shown in Fig. 5. This is emphasized by even a casual comparison of the last half with the first half of these century-long records. Agreement among the widely separated stations is remarkable.

Fig. 6 is reproduced from a paper entitled, "The Composition of the Atmosphere through the Ages," by Prof. G. S. Callendar, Imperial College of Science, London, England, published in the *Meteorological Magazine* for March, 1939. It shows for Europe a general trend to higher temperatures since the turn of the century in accord with findings in the Western Hemisphere.

For purposes of comparison we have reproduced Prof. Callendar's graph in Fig. 7; plotted in conjunction therewith is a composite annual temperature curve

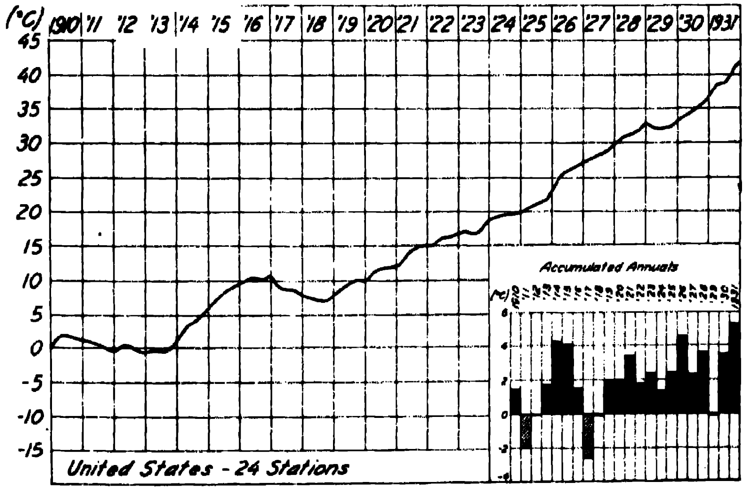

FIG. 8. Accumulated monthly departure from normal temperature, 1910-31.

for the United States, and another for a single station (Capetown) in South Africa. The agreement among these that there has been in recent years, especially since the turn of the century, a very definite trend to higher temperatures, is impressive. It will be noted, however, that the rise has been more pronounced in the United States than in either Europe or South Africa.

There is further conclusive evidence that this trend to higher temperature has been general over the globe. Summaries of monthly records published in the *Reseau Mondial*, an international publication containing records for about 400 stations well distributed throughout the world, for the 22 years from 1910 to 1931 for which the publication is available, show that for this period the world as a whole had subnormal temperatures in only two years, approximately normal in three, and considerably above normal in all the other years. Thus, 80 per cent of the years had decidedly above normal temperature (see Fig. 8).

Geologic Temperature Recorders

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Introduction

A quantitative knowledge of the conditions of formation of minerals and rocks—the temperatures, pressures and concentrations involved—is naturally a matter of much concern to the geologist. At times he is able to view certain processes of mineral formation in progress and can make direct measurements of some of the conditions with the aid of the various devices that have been developed for such purposes, usually by workers in other branches of science or technology. For the measurement of temperature, which is the variable here under discussion, a great many devices are available, but they uniformly depend upon one broad principle. The known rate of change with temperature of some property of a substance, such as volume, electromotive potential, or radiation, serves as a measure of temperature. Various instruments for the direct measurement of temperature have been used by the geologist and he has thus come to know something of the temperatures of flowing lavas, of fumaroles, of hot springs, and of other geologic activities taking place at yet more moderate temperatures.

Some of the contributions to this Symposium will deal with such observations, but it is not to these direct measurements made upon materials in process of change that attention is here directed. For measurements in connection with many technological or natural processes it may be inconvenient to have an observer continuously present, and it has proved possible to construct instruments which will furnish information as to the temperature. These vary from elaborate devices which provide a complete, continuous record of the temperature and have been called recorders, to the other extreme, which furnish only information as to the maximum or minimum temperature attained and are ordinarily called maximum or minimum thermometers. In reality they are, just as definitely, recorders. It need hardly be said that, whether of the elaborate type or the simplest type, recorders depend for their use upon a foreknowledge of the change of some property with temperature. The simple maximum or minimum thermometer merely records the maximum extent of this change in the one direction or the other. In this respect geologic temperature recorders are of the same character as the simplest type of recording instrument, but in other respects they are very different; indeed they are not instruments at all.

It is manifestly not merely inconvenient but altogether impossible for the geologist to be present during most geologic processes, especially those that took place in the remote past. Any record of temperature for these completed processes will be obtained, not by direct observation nor yet through the agency of any man-made recording device, but rather by seeking in the rocks themselves internal evidence of the temperatures attained. Such evidence must come from ascertained facts regarding the effect of temperature upon various physical properties of the minerals of the rock and upon physico-chemical properties of the mineral assemblages. Minerals are the geologic temperature recorders.

Nearly all man-made devices for determining temperature depend upon the measurement of some property which varies *continuously* with temperature. Occasionally it is possible to use some such property in the estimation of geologic tem peratures. Thus the change of volume which has occurred during the cooling of liquid inclusions in crystals, as determined by the relative volume of liquid and its associated gas bubble, has been taken, under certain assumptions, as a measure of the drop in temperature, from which the temperature of envelopment of the liquid by the crystal is readily obtained. Likewise the change of solubility of certain salts precipitated from such fluid inclusions, as determined by the relative quantity of salt and solution, may be a measure of the fall in temperature. Estimates of temperature based upon such considerations have but little reliability. They involve too much unverified assumption as to the initial condition of the materials and too little exact knowledge of the temperature coefficients of volume and solubility of such materials.

It is rather to *discontinuous* changes of properties consequent upon change of temperature that we must turn for indications of temperature in geologic processes. The discontinuous changes are those which ordinarily accompany change of phase, such as melting, boiling, inversion and others. There is, of course, nothing novel in such procedure. In ordinary thermometry use is made of these discontinuities of properties accompanying change of phase; indeed, the whole thermometer scale is referred to a number of fixed points; the melting point of water, the boiling point of water, the boiling point of sulfur and so forth. The devices depending upon *continuous* changes of properties serve only to furnish arbitrary subdivision of the intervals between these fixed points. Geologic thermometry is therefore fundamentally of the same character as ordinary thermometry; both use as reference points the temperatures of phase changes. In ordinary thermometry it is possible to choose convenient and well-behaved substances as those whose phase changes are to constitute the fixed points. Here the geologist is at a decided disadvantage. His temperatures must be referred to possible phase changes in the substances actually present in rocks. In addition there is, in geologic thermometry, no means of subdividing the intervals between the fixed points. The intervals should therefore be as small as possible. Ideally the geologist should know the temperatures of all the phase changes of all minerals; and, although the goal is far from attainment, such knowledge is being gradually accumulated through laboratory studies of the so-called thermal properties of minerals.

What a happy circumstance it would be for the geologist if the melting, inversion, and boiling phenomena of a substance were really adequately described by that designation, thermal properties. Unfortunately they are thermodynamic properties. In all these changes there is involved, in addition to a thermal factor, a work factor, because a change of volume accompanies the change of phase, and the magnitude of the work factor depends upon the applied pressure. The temperature at which the phase change occurs therefore varies with the pressure, the effect of pressure being expressed quantitatively in the well-known Clausius-Clapeyron equation. The variation is a matter of small concern to the physicist seeking to establish a series of fixed points on a thermometer scale, for he can define a point in terms of an arbitrary and convenient pressure, whereupon the temperature of the phase change becomes indeed a fixed point. But the geologist must take things as he finds them. He has no control over the process whereby minerals were produced, and in seeking to use the temperature of a change of phase as a "point" on a thermometer scale he must have due regard for the effect of pressure on the temperature at which the change occurs. It is sometimes possible to estimate with sufficient accuracy the superincumbent load under which mineral formation or transformation occurred and thus to make appropriate correction to the temperature as measured under the ordinary pressure, but it is always desirable to place principal reliance upon phase changes in which the volume change is small and the effect of pressure correspondingly small. Thus equilibria between solids or between solids and liquids are generally to be preferred to equilibria involving the formation of a gas.

Having gained, by laboratory investigation, a knowledge of temperatures of various equilibrium phase changes for a wide range of mineral substances, and having thus established his "fixed" points, the geologist puts them to work by examining rocks and attempting to decide from internal evidence whether its materials have passed through any of these points. The nature of the evidence varies and can only be discussed in terms of specific examples. It is always concerned with the answer to the question whether or not a certain temperature has been attained and thus is, as already pointed out, not unlike the evidence furnished by a maximum (sometimes a minimum) thermometer. With this preliminary discussion of the general character of natural temperature recorders in geology we may pass to a consideration of some of the "fixed" points and their utility.

Melting Points

The melting point of any crystalline substance, at a given pressure, places an upper limit upon the temperature range in which that substance can crystallize at that pressure. To be sure, this is frequently not a particularly useful fact, for the presence of other substances usually lowers the melting point so much that the limitation placed by the melting point of the substance itself is altogether too wide, especially for substances of high melting point. If we consider Table 1, in which are given significant melting points of minerals, we find that there is evidence from other considerations that such minerals as olivine have crystallized in all rocks at temperatures far below their melting temperatures, so far indeed that the melting point is only of secondary importance as an indicator of the maximum possible temperature at which crystallization could have occurred. On the other hand, if we turn to such a mineral as native bismuth, which melts at 271 °C at the ordinary pressure,* we may say that in any deposit containing that mineral we may be sure that the bismuth, and any minerals deposited contemporaneously, were formed (crystallized) below 271 °C; and this may be very useful.

Table 1. Significant Melting Points of Minerals (°C).

Olivine (forsterite)	Mg_2SiO_4	1890
Enstatite	$MgSiO_3$	1557*
Plagioclase (An)	$CaAl_2Si_2O_8$	1550
Diopside	$CaMgSi_2O_6$	1391
Plagioclase (Ab$_1$ An$_1$)		1287–1450
Orthoclase	$KAlSi_3O_8$	1170*
Plagioclase (Ab)	$NaAlSi_3O_8$	1120
Aegirite	$NaFeSi_2O_6$	990*
Pyrrhotite	$FeS+S$	1157–1187
Galena	PbS	1120
Argentite	Ag_2S	842
Stibnite	Sb_2S_3	546
Pyrargyrite	$3Ag_2S \cdot Sb_2S_3$	483
Orpiment	As_2S_3	320
Bismuth	Bi	271
Sulfur	S	119

* Melts incongruently.

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* Bismuth, like ordinary ice and unlike most substances, contracts on melting and its melting point is consequently lowered by increased pressure. At 3000 atmospheres, corresponding with a depth of some 10 kilometers in the earth, it is lowered only to 260 °C.

The limited utility of the minerals of high melting point as indicators of maximum possible temperatures of their crystallization no longer obtains, of course, if the magnitude of the effects of the associated minerals is known. In other words, if we know the melting temperatures and general thermal behavior of mineral assemblages, then the properties of the assemblages can be used in the same manner as the properties of individual minerals, and lower limits can be set to the maximum possible temperature of crystallization. An enormous amount of information is, indeed, now available upon the melting points of mineral mixtures and is used to indicate maximum possible temperatures of formation. It is not possible to present such material in brief compass, and in its details it concerns primarily the geologist rather than the physicist, who can in this connection be interested, for the most part, only in methodology.

Upon occasion the geologist may wish to know, not merely the temperature at which a certain mineral or group of minerals formed, but also the temperature that may have been attained by the liquid or melt from which they formed. Information as to the temperature attained when the melt was (if it ever was) at very great depth in the earth, we may not hope to secure, but upon its temperature when it reached the position in which we now find its products we can reach rather definite conclusions. They come again from consideration of melting points of minerals, not, to be sure, of the minerals formed from the melt, but of the minerals in foreign inclusions that have been caught up by the melt. Small inclusions must attain the full temperature of the liquid and show the appropriate effects. Solution there frequently is, but forthright melting is not common and is displayed only by inclusions made up of the more fusible minerals or mineral assemblages. The evidence points strongly toward the conclusion that the liquids or melts from which rocks have formed were not excessively hot, were indeed in most instances within their crystallization range.

Besides indicating the maximum possible temperature of crystallization of a mineral, the melting point may be regarded also as the minimum possible temperature of existence of a liquid having the composition of the mineral. However, when we find a rock giving every evidence of having formed from the molten state and consisting entirely of one mineral, we should not feel compelled to conclude that it was formed from a liquid which had a temperature higher than the melting point of the mineral. In the case of rocks consisting entirely of olivine, a temperature approaching 1890 °C for the liquid would be indicated by such reasoning; but when we examine inclusions with known thermal properties in such olivine rocks, no evidence is found that they have been subjected to such high temperatures. We are forced to seek an origin for such rocks other than their formation from a liquid consisting entirely of olivine substance. Either the olivine crystals accumulated from a complex melt rich in other silicates which gave it a relatively low melting range, or the liquid, with respect to its silicate content, was substantially of olivine composition, but contained considerable quantities of volatile substances now lost. Upon the relative merit of these two possibilities no general agreement has been reached. It would carry us too far into geologic minutiae to discuss the pros and cons; indeed we have perhaps already strayed too far in that direction for present purposes, but it has been deemed advisable to discuss rather fully the geological significance of some of these melting points before passing on to a consideration of other types of "fixed" points.

Inversion Points

A great many mineral compounds can appear in more than one crystalline form, and the temperature at which two crystalline forms (phases) are in equilibrium is called an inversion point. The most useful "fixed" points in geologic thermometry are inversion temperatures; and their use depends upon the observer's ability to decide (a) which crystalline form of a substance is present in the rock, and (b) whether that form was originally present, or whether it has developed by inversion from another form. Decision upon the first question (a) is nearly always readily made; the second question (b) must at times be left open, but can be answered frequently enough to enable the establishment of definite conclusions. And here it is important to note that inversions may be broadly classified for present purposes into two classes, the prompt and the sluggish. In the former, the substance changes promptly from the high-temperature form to the low-temperature form when the temperature passes downward through the inversion point, and the reverse change takes place as readily when the temperature change is in the opposite direction. Obviously, with such a substance, if crystallization takes place above the inversion point, it will invariably give the high-temperature form, and if below the inversion point the low-temperature form will result. Obviously, too, the form observed upon examination of the rock at room temperature will always be the low-temperature form, and we can use the inversion point as a recorder of temperature only if we can decide by study of this low-temperature form whether it is original or whether it was formed by inversion from the high-temperature form.

The sluggish inversions present a different picture. The high-temperature form of a substance having such an inversion may be cooled through the inversion point without appearance of the low-temperature form, and it may be necessary to hold the temperature a little below the inversion point for a considerable period before inversion occurs. If, instead, the temperature is permitted to fall rapidly to room temperature, the high-temperature form will persist indefinitely. If the low-temperature form is heated, its temperature may rise above the inversion point without appearance of the new form; but it is the universal experience that there is much less lag in the rising-temperature direction. From these observations, which are of course made in the laboratory under controlled conditions, it might be supposed that the sluggish inversion would be more serviceable than the prompt as a temperature recorder. The finding of the high-temperature form of a mineral substance in a rock might be regarded as indicating that the rock formed above the inversion temperature, and the presence of the low-temperature form as indicating formation below the inversion temperature. Unfortunately the situation is not so simple, for it has been observed in many substances with a sluggish inversion, and it is probably true of all such, that the high-temperature modification can not only persist at low temperatures but can actually form at these temperatures. The high-temperature phase thus furnishes no indications as to temperature unless there is clear evidence that the substance was originally in the low-temperature modification and was transformed into the high-temperature modification. There is then, of course, undoubted evidence that the temperature of the material has been raised to a point above that of the inversion. In all the materials studied the low-temperature phase has not been observed to form above the inversion, and probably cannot. The presence of that form is therefore a definite indication of crystallization below the inversion temperature, provided the evidence is clear that the low-temperature modification was not formed secondarily by inversion of the high-temperature modification; and decisive evidence on that question is usually forthcoming.

With this amount of general discussion of the character of inversion points and their utility as fixed points in geologic thermometry, we may pass to consideration of a few examples. The substance SiO_2, by reason of its widespread occurrence and its crystallization in a number of different modifications, is especially useful. There are four stable forms and therefore three inversions which are as follows at the ordinary pressure.[1]

low quartz ⇄ high quartz	573 °C
high quartz ⇄ tridymite	870 °C
tridymite ⇄ cristobalite	1470 °C

The effect of pressure on the first inversion has been measured.[2] It is raised 21.5° by a pressure of 1000 atmospheres, which corresponds to a depth of some 2.5 miles in the earth. The effect of pressure on the second inversion can be calculated only from approximate values of the heat effect and volume change, and appears to be significantly greater than the above and in the same direction. The third inversion lies at too high a temperature to be of any significance as a fixed point; but since cristobalite is a well-known natural mineral, the conditions of its formation must be considered. The first inversion is of the prompt variety, the other two are sluggish. They are therefore to be used somewhat differently; and it may be added here that inversions, like melting points, are used for two purposes, namely, to indicate temperatures of initial formation and to indicate temperatures to which immersed inclusions were heated.

By virtue of what has been said of sluggish inversions it is plain that cristobalite and tridymite should be able to form at low temperatures; indeed they do in the laboratory, and they cannot ordinarily be taken as indicators of high temperature. In many occurrences there is clear evidence from other sources that they were formed at moderate temperatures far below their stable ranges. Occasionally the one or the other is found as one of the minerals of a foreign inclusion in a magma and has characters indicating its formation by inversion from quartz. In such cases the definite conclusion can be drawn that heating above at least the 870° inversion has occurred; but the formation of cristobalite cannot be taken to indicate heating above 1470° because quartz has been observed in the laboratory to change directly to cristobalite below 1470° and without passing through the intermediate stable form tridymite. On the other hand, an inclusion which furnished evidence that tridymite was transformed to cristobalite would necessarily have been heated above 1470°, but such temperatures are unknown in geology except perhaps in connection with two phenomena, the formation of fulgurites by lightning and the formation of impact craters by meteorites, phenomena which are, presumably, as much geologic as meteorologic or cosmic. In some of these instances silica has thus been heated not merely above its 1470° inversion but above its melting point at 1713°, possibly above its boiling point.

In geology proper it is the lowest stable inversion of silica that is the most serviceable. This change, involving high and low quartz, takes place at 573° and is of the prompt variety. All quartz as viewed at low temperature is therefore low quartz. The problem is to determine whether it was ever high quartz, in other words whether it gives evidence of having passed through the 573° inversion and therefore of having been formed above 573°. A number of criteria are available, based on the change of crystal form and of volume which are known to occur at the inversion. They will not be enumerated here, but by their aid it can sometimes be decided whether or not the quartz was formed above 573°. It is a very useful reference point for the crystallization of many rocks and mineral deposits.

We thus see that, although persisting metastably and at times even formed metastably, nevertheless all the principal forms of SiO_2 are found in nature, even those which are stable only at quite high temperatures. Not all substances show like relations. There are a number of substances with known high-temperature forms which have never been observed in these forms in nature. Among these is the mineral wollastonite,[3] $CaSiO_3$. At approximately 1140° it inverts to a different form, pseudo-wollastonite, which is known only in laboratory or technologic products. The inversion is rather sluggish, too, and it seems inevitable that pseudo-wollastonite would have survived in some rocks if it had ever formed. Or again, if some wollastonite is formed secondarily by inversion from pseudo-wollastonite, it should in at least some instances give evidence of that fact. No such evidence has been found. It is difficult to avoid the conclusion that in no rocks has the crystallization of $CaSiO_3$ taken place above 1140°, nor yet has any rock, occurring as inclusions in a melt and containing wollastonite, been heated to a temperature as high as 1140°. The substance $NaAlSiO_4$ furnishes another example of the same general relations. In the laboratory it is transformed at 1248° to a modification which is quite unknown in nature.[4] The same reasoning applies to it as to the substance $CaSiO_3$. We are here concerned with a somewhat higher temperature, but there is confirmation of the conclusions reached on the basis of $CaSiO_3$. These and other substances with similar relations furnish indisputable evidence of the comparatively moderate temperatures attained in geologic processes in the accessible part of the earth, even in the highest-temperature stages of these processes.

On the other side of the picture we have a number of substances which invariably give evidence of having cooled through an inversion point and therefore of having been formed above that inversion temperature. The evidence is ordinarily the presence of a complex twinning which is known to develop at certain inversion points. The majority of these inversions lie at comparatively low temperatures so that, although the minerals concerned always form above the inversions, in no particular do they furnish evidence contradictory to the evidence cited above of the moderate temperatures of geologic processes. Among the substances in this class may be mentioned argentite (Ag_2S) with an inversion at 189°, boracite ($Mg_6B_{16}O_{30} \cdot MgCl_2$) at 265°, cryolite ($Na_3AlF_6$) at 570°, leucite ($KAlSi_2O_6$) at 603°. The last of these is at a comparatively high temperature yet it appears that natural leucite has nearly always, if not always, formed above this temperature.*

Phase Equilibria in Polycomponent Systems

For the most part only phase equilibria in systems of a single component have been discussed as "fixed" points. In each case they represent univariant equilibrium and, as already pointed out, are fixed only when the pressure is fixed or known. Any equilibrium may, theoretically at least, be equally useful, however great the number of phases involved, provided that the reaction is univariant, that is, that the number of phases exceeds the number of components by one. Some hint of the use of such equilibria has been given in the mention of melting temperatures of mineral assemblages. There are other kinds of equilibrium between a number of phases that may be of service, especially for the establishment of temperatures of mineral development in metamorphic rocks. Some of the reactions involve a gas phase, and here the effect of pressure on any univariant equilibrium is so great that, unless there is field evidence which determines the approximate value of the pressure, the temperature of the reaction may be set only within rather wide limits. Even when the actual magnitude of the pressure is quite unknown, reactions of this type may have some temperature-orienting value, especially where different reactions have taken place in different parts of a rock mass so disposed that all parts of it must have existed under substantially the same pressure.

* Leucite, and indeed some of the other substances above listed as being in this class, may sometimes show twinning even when formed in the laboratory below the inversion temperature; but such twinning can usually be distinguished from that originating during inversion and has not been definitely recognized in the natural mineral.

The dissociation of carbonates with evolution of CO_2 is a reaction of the type under consideration. The dissociation pressure of calcite ($CaCO_3$) has been measured at temperatures up to those of melting, and in the light of this knowledge it is not surprising that examples of this reaction are not found in nature. To be sure, $CaCO_3$ dissociates freely, with formation of CaO and CO_2 at a temperature of 900° when the pressure is only 1 atmosphere, but the weight of only 40 meters of rock is sufficient to prevent dissociation at 1100°. To such a temperature limestones have probably seldom been heated even at much greater depths.

Other carbonates such as magnesite ($MgCO_3$) and dolomite ($CaMgC_2O_6$) have higher dissociation pressures at corresponding temperatures, and their dissociation has occurred in nature. Magnesite is not a common mineral, but dolomite is common; and geological evidence points to its dissociation when heated with formation of periclase (MgO), calcite and CO_2 according to the equation.

$$CaMgC_2O_6 \rightleftarrows MgO + CaCO_3 + CO_2$$

From laboratory experiments something is known of the CO_2 pressures of this univariant reaction at various temperatures.[5] If there is field evidence revealing the depth of burial of a dolomite at a time when it was heated, say by contact with an igneous intrusive, it may be possible to reach some conclusion as to temperature, usually the fixing of a temperature above which it could not have been heated.*

Calcite itself reacts with certain other minerals, with evolution of CO_2, at temperatures far below those at which simple dissociation of calcite will occur. Thus calcite and quartz react according to the equation

$$CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$$

This is a univariant equilibrium and the pressure of CO_2 has thus a definite value for a given temperature. In some quartz-calcite rocks this reaction has failed to occur; in others it has occurred with formation of wollastonite ($CaSiO_3$); and this difference of behavior is observed at times in adjacent parts of the same rock mass, from which facts it may be possible to reach conclusions as to the relative temperatures prevailing. The actual temperatures could be deduced only on the basis of experimental determination of the pressures of CO_2 for this reaction at various temperatures. No satisfactory results have been obtained. Calculations have been made of the values of the pressure at various temperatures assuming the validity of the Nernst heat theorem.[6] These can give no more than a rough approximation to the truth, but until something better is available they are not without some value. The depth of burial being known, the failure of the attainment of a certain temperature is recorded in the rock by the failure of this reaction, that is, by the persistence side by side of calcite and quartz. The quartz-calcite association would be one of the more valuable temperature recorders if adequate knowledge were available of the p, t curve of this univariant reaction.

In addition to these reactions occurring in rock metamorphism and involving a gas phase, there are a great many reactions in which no gas phase is concerned. An example in which there are four reacting phases is furnished by the equilibrium between wollastonite and anorthite on the one hand and garnet and quartz on the other, according to the equation

$$2CaSiO_3 + CaAl_2Si_2O_8 \rightleftarrows Ca_3Al_2Si_3O_{12} + SiO_2$$

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* The experimental values indicate that even at a depth of 0.5 kilometer dolomite would be dissociated by heating to a temperature of about 600°.

Since there are three components the reaction is univariant, and has a definite p, t curve; but for it and most other reactions between a number of phases the information needed for the construction of such curves is lacking, and knowledge regarding the temperature-pressure relations is available only in so far as field relations permit their placing relatively to some of the reference points already discussed. Many such reactions are, however, capable of furnishing independent fixed points and no doubt will so function as experimental results are accumulated.

There is one unusual type of rock for which there is a great volume of experimental results applicable to the temperatures of formation of the constituents. This rock is that which occurs as beds of potassium salts such as the Stassfurt salt deposits, the origin of which is still, in some of its details, an open question. Complex equilibria between a considerable number of phases are here concerned, and there are certain individual phases and again certain phase assemblages that have minimum temperatures of formation. These are useful temperature recorders. Among them we may mention only the individual phase vanthoffite, $MgNa_6(SO_4)_4$, with a minimum temperature of formation of 46° from the complex solutions, and the assemblage sylvite (KCl), kieserite ($MgSO_4 \cdot H_2O$), and halite (NaCl) with a minimum formation temperature of 72°. Since such temperatures cannot be supposed to have existed during the evaporation of the natural brines, it must be concluded that the deposits have been subjected to these higher temperatures as a result of burial beneath a significant thickness of other strata, with consequent metamorphism (recrystallization) and formation of the higher temperature phases and phase assemblages.

The experimental investigation of the potash salt equilibria was carried out largely by Van't Hoff and his associates, and it is to him that we owe the expression "geologic thermometer."

Conclusions Regarding Temperatures of Geologic Processes

In their full details the conclusions reached as to temperatures of various geologic processes by the use of the various recorders are the concern of the geologist, but some general conclusions may be mentioned here.

The temperatures of magmas (molten rock) have seldom if ever exceeded 1200 °C when they have arrived in that part of the crust of the earth which becomes accessible to observation as a result of erosion. Most magmas have probably not exceeded 900 °C and some, especially those rich in alkali-aluminous silicates, have had temperatures little in excess of 600 °C. The temperatures of consolidation (crystallization) of the igneous rocks formed from these magmas are but little lower than the temperatures of the magmas themselves; in short, the magmas carry little superheat. The temperatures of crystallization are highest for the rocks rich in lime-magnesian constituents and lowest for those rich in alkali-aluminous silicates and free silica. The temperatures of crystallization of pegmatites, which are formed from residual magmas especially rich in water and other volatile substances and are one of the storehouses of the radioactive elements, lie in the neighborhood of 573 °C. Mineral veins, formed from the residual aqueous solutions after crystallization of the main rock constituents, were deposited at temperatures in part approaching those of pegmatites and extending from this range down to the temperature of boiling water and even lower, with characteristic minerals at each stage.

So much for the rocks and mineral deposits formed in descending temperature stages of the geologic cycle. There are, in addition, rocks and mineral deposits formed under conditions attended by rising temperatures. Sediments and other materials formed at the surface of the earth and at the temperatures there prevalent may be buried under later accumulations, and as a result of such burial they experience a rise of temperature. New minerals sometimes form, the original minerals invert to high-temperature forms and some assemblages probably suffer a certain amount of selective fusion. The extreme of reheating is experienced when such materials are immersed in molten magmas, in which case the more susceptible are themselves melted; but the indications are that even under these most extreme conditions rock materials have probably never been heated above 1150 °C.

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Temperatures of Volcanoes, Fumaroles, and Hot Springs

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Igneous rocks formed during volcanic activity are designated as extrusive, and those which on the basis of field evidence were injected under the earth's surface are called intrusive. Both types have many chemical and mineralogical characteristics in common, and we infer from the study of the extrusive rocks that heat was involved in the formation of the intrusives. Laboratory investigation of the rocks and of their mineral constituents has fully confirmed this idea and has given rise to the term *geological thermometer*[1] which in itself is a recognition of the importance of temperature in these natural processes. The temperature of formation in a given environment is now known for many minerals, and it serves as an important aid in determining the temperature that prevailed when igneous rocks were formed.

The obvious emission of heat associated with volcanic activity and with the related fumarole and hot-spring manifestations has provoked much speculation as to its origin. The determination of temperature has naturally been the concern of all investigators of these phenomena. The lack of suitable instruments for measuring high temperatures caused the earlier workers to confine their attention to hot springs. They had to be content with describing the heat intensity of volcanic activity in terms of the heat effects produced in known industrial processes. Even though suitable instruments are available at the present time, the physical difficulties involved in approaching an active volcano, and the hazards that must be overcome make it difficult to obtain the valuable information afforded by temperature measurements. Nevertheless, a fair amount of data has been obtained in a few areas where conditions are favorable for such work.

It is the purpose of this paper to outline the methods used and the results obtained when temperature measurements are made at hot springs, geysers, fumaroles, and volcanoes.

The measurement of temperature at hot springs is now a comparatively simple procedure. The earlier workers used an ordinary mercury thermometer and had no difficulty in showing that the temperatures ranged from a few degrees above the surrounding air to the boiling point of water characteristic of the altitude at which the spring is found. It is now recognized that not all hot springs are immediately related to some buried igneous body, for it is quite possible that surface water may travel fairly deep into sedimentary rocks and become heated to the temperature prevailing at these depths and reappear at some distant point as a hot spring. It is not probable, however, that this type of hot spring will attain the temperature of those intimately associated with an igneous intrusion.

The geological evidence afforded by the igneous materials deposited in the Yellowstone Park area indicates that the source of heat in the hot springs and geysers of this region is in a buried igneous intrusion. The systematic measurements of temperature of the hot springs and related thermal activity carried out by Allen and Day[2] revealed the fact that many of the springs contained water that was several degrees above the boiling point characteristic of the altitude of the location. It could easily be shown that the amount of dissolved material could not have raised the boiling point by more than 0.2 °C. These superheated springs are potential geysers. Day and Allen were led to the conclusion that surface waters were heated by gases escaping from a buried hot magma, thus giving support to the idea inferred from the geological investigations.

It is quite natural to believe that the temperature of wells drilled in such an area should show an increase with depth. Several decades ago the Italian scientists sunk wells in the thermal area of the Lardarello[3] district and found that the temperature steadily increased until steam at approximately 120 °C appeared with explosive violence. Many more steam wells have been drilled since then, with the result that the area is now an important source of power. Similar investigations were carried out in Java,[4] in California,[5] and for purely scientific reasons by Fenner[6] in the Yellowstone Park area. The appearance of superheated steam at elevated pressures in these wells furnished contributing evidence for the belief that the source of heat in the hot springs and geysers was located in a buried igneous mass. There are a surprisingly large number of thermal areas associated with some form of igneous activity where one can quite safely drill for superheated steam with the definite assurance of obtaining a large continuous supply; its economic utilization is, of course, quite another matter. In drilling such a well an experienced man can tell from the rate of increase in temperature when the well is about to be brought in. A maximum thermometer is very useful for this purpose.

The "maximum" thermometer is generally used for all preliminary work in areas of relatively low thermal intensity. The 6-inch armored type is short enough to permit in most cases complete immersion and thus avoid the usual stem correction. It can be obtained in several ranges such that the interval from 0 to 220 °C is covered in three steps. This permits graduation in 1.0° intervals and the estimation of 0.5°; this accuracy is adequate for most investigations in the field. The thermometers should, of course, be calibrated before taking them into the field, especial attention being paid to the amount of contraction of the mercury thread that occurs between the time of withdrawal and actual reading. This contraction may amount to as much as 1.0° in the vicinity of the 200° range. It is wise to reject thermometers with a greater contraction than 1.0°; when this is the case, the thread of mercury above the constriction shows a tendency to move freely if the thermometer is held in other than the vertical position. It is possible to obtain maximum thermometers with a much higher range than 220 °C, but it has been found that the correction which must be applied for the contraction of the mercury after withdrawal from the source of heat may be as high as 2.0 °C. Then, too, it is very difficult to shake down the thread in these higher range thermometers.

The surface drainage in many thermal areas contributes a large portion of the emitted water and steam, and it is for this reason often desirable to note if there are seasonal changes in their temperature. For such purposes a recording thermo-element pyrometer is almost essential. The junction must obviously be protected against mechanical shock and chemical activity.

The steam wells referred to above are in a sense artificial fumaroles and represent a higher thermal intensity than that characteristic of hot springs. Fumaroles are, as the name implies, chimneys or holes in the ground from which steam and other vapors are escaping. They are usually considered to be the waning phase of volcanic activity. This concept, however, may lead to erroneous conclusions concerning the potentialities of the igneous material in the hearth of the volcano. There are volcanoes such as Fuego[7] in Guatemala and Merapi[8] in Java where fumarolic activity gave the impression of extinction, but several years later violent eruptions gave proof that the volcanoes were only dormant. Systematic temperature measurements of the escaping gases should prove useful in following the growing thermal intensity at such intermittently eruptive centers. The physical difficulties usually involved in approaching these vents, the lack of organized research and lack of funds, and the appearance of volcanic activity only at long intervals of time are adequate reasons why volcanologists have not made such systematic investigations. A well organized observatory is practically essential for such work. The information sent out by the observatories at Vesuvius and at Kilauea is largely responsible for the fact that we have more detailed knowledge of these volcanoes than of any others.

When the fumaroles are not located at or near an active volcano they may be an indication of waning activity, but in such cases the geological evidence permits one to infer the presence of a more or less deeply buried mass of intruded hot material. The Yellowstone Park and the area of California called "The Geysers"[9] should be cited as examples.

The fumarole activity in the Valley of Ten Thousand Smokes[10] continued from its first appearance in 1912 to about 1923. During this period the Valley was probably the most extensive fumarole area of historic times. Systematic determinations of temperature were made in 1917, 1918, and 1919. They ranged from a few degrees above the prevailing air temperature up to 645 °C. The persistence of steam temperatures as high as 645 °C over a period of seven years, together with the fact that the fumaroles are located in a huge mass of pumice extruded during the eruption of 1912, gave rise to the belief that the heat was derived from a relatively large body of magma that had intruded under the old Valley floor.[10a] Comparison of the measurements made in 1919 with those made in 1917 and 1918 showed that the thermal activity was waning, and it could also be shown that much of the water that appeared as steam was derived from surface drainage. The prediction[11] was made that hot springs would be the dominant type of thermal activity within a few years' time. This decline in intensity was noted in 1932.[12] As a matter of fact, there is little thermal activity now to be seen at the surface.

Not all thermal areas associated with an igneous intrusion are so ephemeral as that of the Valley of Ten Thousand Smokes. The activity at Yellowstone Park, for instance, has continued for thousands of years. It would seem that the depth at which intrusion takes place, the volume and temperature of the hot material. and the amount of surface waters that reach it in a given time are involved in determining the length of time that thermal manifestations will be obvious at the surface.

When temperatures higher than those determinable with a maximum thermometer are encountered, a portable potentiometer and appropriate thermoelement are used. This instrument can, of course, be used for lower temperatures, but the handiness of maximum thermometers and their adequate accuracy make them ideal instruments for preliminary investigations. Indeed, considerable information as to thermal intensity can be obtained by an experienced observer by noting the appearance of the incrustations in and around the throat of a fumarole and of the steam issuing from it. When a deliquescing salt is found right in the vent, then the temperature is not above the boiling point of a saturated solution of the salt, which usually means within a few degrees of 100 °C; the obvious condensation of the steam in the throat of the vent furnishes additional evidence that the temperatures are relatively low. It often happens that no condensation takes place within the immediate vicinity of the vent; nevertheless a dense cloud of steam is emitted. If a stick is inserted in the opening and no charring is observed after about five or ten minutes, it is safe to infer that the temperature is in the neighborhood of 150 °C. If light charring occurs within about five minutes, a temperature of about 200 °C may be assumed. If charring occurs within a few seconds, temperatures over 350 °C. prevail. Under such conditions the vapor in the immediate vicinity of the vent will usually have the appearance of a bluish haze, and hard, cemented, often clinker-like masses of incrustations and rock alteration products will be found around the opening. Such rough appraisals of temperature serve the useful purpose of deciding whether a maximum thermometer or a pyrometer should be used.

It was stated above that a portable potentiometer equipped with a thermoelement is an excellent pyrometer for use in the field, especially in fumarolic areas where high temperatures are indicated. A calibrated Chromel-Alumel thermoelement of No. 22 B. & S. gage can be wound on a double reel and has the flexibility required for insertion in narrow cracks and irregular-shaped openings. The junction with properly insulated leads may be incased in a metal tube, but this is rarely necessary and often lowers the flexibility of the instrument. It is important, of course, to insure complete separation of the leads in order to avoid short circuiting. On one of the expeditions to the Valley of Ten Thousand Smokes[13] small glass beads were strung on the leads and thus insured the flexibility desired. The thermocouple was tried out at a fumarole where the maximum thermometer had revealed a temperature around 200 °C. Much to our surprise, the temperature as calculated from the millivoltmeter readings rose steadily to almost 600 °C. No attempt was made to keep the beaded wires separated, and inspection showed that water had condensed on the beads and bridged the leads. It was known that the emanations contained small amounts of acid gases, and their solution in the condensed water was sufficient to produce electrolytic effects which gave the absurd readings. The leads were thereafter separately mounted on short sticks and no further trouble was experienced. At the place where the junction entered the opening the leads were insulated with "Pyrex" or silica tubing of adequate length. The ground near a vent is quite often permeated by hot, steamy vapors; when such conditions prevail it is obviously necessary to place the potentiometer on the nearest cool spot, which may be as much as 50 feet away. The small dry batteries with which the instruments are equipped have a rather limited life when exposed to the humid atmosphere characteristic of fumarolic areas, but this can almost be doubled if they are immersed in melted paraffin before they are taken into the field.

Many fumaroles are located in the craters or on the slopes of volcanoes, which are usually at a considerable distance from what one is pleased to call civilization, and it is therefore necessary to take along replacements such as spare thermometers, indicating galvanometers, and batteries. It is essential that the operator know his potentiometer well enough that he can take it apart and make such repairs as may be required. Trouble shooting is an expressive term and the investigator in the field should be adept at the art. It not infrequently happens that it is necessary to work on a steep, wind-swept slope. Adaptability of the investigator and flexibility of the instruments are here of great importance. Measuring devices must be set up on the windward side, but the air currents will not always stay put, so to speak, and in consequence it is quite essential to move out of the way quickly when there is a sudden change in the direction of the wind, else severe burns and, in acid areas, severe irritation of nose and throat will result.

The measurement of temperature of the fumaroles, together with the chemical study of the incrustations, has made it possible to point out the importance of vapor-phase activity in producing concentration at the surface of many constituents that were present in the parent magma only in minute concentrations.[14] This form of activity was especially characteristic of the Valley of Ten Thousand Smokes. Similar conditions were observed at the fumarolic area associated with the volcano of Papandajan in Java.[15] Temperature measurements of two fumaroles separated by about 200 feet revealed that the steam and other vapors escaped from the one at 110 °C and the other at 350 °C. Great cones of pure sulfur were found at the former, and tellurium, selenium, and small amounts of sulfur and arsenic were found at the other; yet the gases escaping from the hotter fumarole contained much sulfur and but little of the other constituents. This differential concentration of the elements is obviously conditioned by the well-known difference in vapor pressure of these elements at the prevailing temperature. The vapor pressure of sulfur is small but appreciable at 110°, whereas that of tellurium, selenium, and arsenic sulfide is vanishingly small by contrast. The sulfur is promptly precipitated at the surface, but the other constituents never reach it. At 350 °C the vapor pressure of sulfur rises rapidly, and that of tellurium, selenium, and arsenic just becomes appreciable. The sulfur for the greater part is volatilized into the atmosphere; the other constituents of much lower vapor pressure are promptly deposited around the vent.

The deposition of secondary products through vapor-phase activity is often very pronounced at fumaroles located in a lava flow. Temperatures may here run as high as 700 to 800 °C. In spite of the ephemeral character of such fumaroles, their study has yielded much information concerning the minerals concentrated at the surface and the role played by temperature throughout their development. It is gradually becoming apparent that the investigation of the surface manifestations of volcanism, together with the laboratory study of the alteration products formed during this period, will permit the drawing of logical inferences with respect to the segregation through vapor phase activity of mineral species in the intrusive magmas.

The intensive form of thermal manifestation characteristic of volcanic activity offers more serious obstacles to the taking of temperatures than either hot springs or fumaroles; yet it is most important that such measurements be made because the temperature of the rapidly extruded lava or fragmental material closely represents the thermal intensity that exists within the hearth of the volcano. It is not the purpose of this paper to discuss the various types of volcanic activity, but it should be stated that the dominant type of the present day exhibits explosive tendencies and that only rarely is it unaccompanied by obvious heat effects. In some cases only reheated fragmental material is extruded; in others, the explosively emitted hot fragmental material is followed by or accompanied by the extrusion of more or less consolidated flows of lava. Not all volcanic activity is accompanied by explosive activity, as is shown by the relatively quiet emission of basaltic flows at Kilauea, at Batoer on the Island of Bali, and at the rift volcanoes of Africa.

Very few determinations of the temperature of an igneous extrusion have been made up to the present time. The remoteness of the volcanic disturbance, its fortuitous occurrence, and its usually ephemeral character are obvious reasons why this should be so. The best determinations have been made at volcanoes that have shown fairly continuous activity, and especially at those that have been active long enough to justify the expense incurred by the erection of an adequately equipped observatory or by the sending out of an adequately equipped expedition. The term "adequate" must be taken with a grain of salt, for the present state of our knowledge concerning the requirements of such an observatory or expedition, and the lack of available funds leave considerable room for doubt as to what the term includes. *When a volcano is in the explosive stage, observations must be made at a distance* of a kilometer or more, and the only method at present available for making estimates of temperature is some form of optical pyrometer. A simple and easily portable device using the principle of matching either color or brightness would be of great assistance to the worker in the field who, more or less by accident, is confronted with a volcanic eruption. Such a device would have been helpful during the 1932 explosive eruption of Fuego in Guatemala.[16] No fresh lava was extruded, but instead only reheated fragmental rock that had remained in the throat after the eruption of 1883. At one stage of the activity this fragmental material poured over the rim of the crater during the night and had an obvious dull red glow. The temperature was probably around 550 °C. This is, however, only a crude estimate, but an observer who has standardized his eye, so to speak, by viewing heated objects with an optical pyrometer of the disappearing filament type becomes accustomed to judging temperature by color and brightness.

No matter what kind of optical pyrometer is used for estimating the temperature of materials extruded during explosive activity, the absorption effect of the dust in the atmosphere must be taken into consideration. The writer was lucky enough this year[17] to use with fair success a portable optical pyrometer of the disappearing filament type at the volcano of Santiaguito in Guatemala. It had been previously noted that at night the hot lava had a clear red color which indicated a temperature of about 700 °C. This is close to the lower limit at which the disappearing filament pyrometer is usually employed. The suggestion was made by Messrs. H. T. Wensel and W. F. Roeser of the National Bureau of Standards that the portable pyrometer could be calibrated down to 550 °C, provided all glass filters were removed. The writer is indebted to these gentlemen for the loan of such an instrument and for supplying the calibration curve between the limits of 550 and 950 °C. It is quite difficult at first to match the dull red of the test object at 550 °C with that of the filament; but visual acuity improves with practice, and readings made under test conditions can be duplicated within ±5 °C. It is doubtful, however, whether it is possible to make brightness matches at this temperature of a natural object such as a heated lava. It must be remembered that there is a fair amount of light diffused from the starlit sky. Fortunately, very little of this light is reflected by the coarse-textured lava peculiar to Santiaguito, and for reasons given below it was believed that blackbody conditions were closely approached. The lava is intermittently extruded near the top of the volcanic dome as an exceedingly viscous mass of minerals entrapped in a small amount of mother liquor. Such materials congeal quickly after emergence, and the heat effect as shown by color is seen only during the few minutes that elapse just before emergence of the lava blocks and their final deposition on the slopes. Many observations had to be made because only rarely was the image of the glowing patch large enough to offer a good background to the filament, and only rarely did the glow persist long enough to permit a satisfactory matching of brightness; but each effort represented a closer approach to what proved to be the maximum temperature. Several times it was possible to sight on glowing patches in a deep recess, and hence it is believed that blackbody conditions were approached. An area was found from which the lava was intermittently but persistently extruded, and after obtaining approximate settings on the millivoltmeter it was possible with the aid of an assistant to follow the increase in temperature from apparent blackness, around 550°, to 725 °C, which was the highest temperature observed during the eruptive process. In several observations, the telescope was removed and the filament tube directed towards a black area just to one side of the glowing spot. The brightness of the filament was thereupon matched with that of the glow on the volcano. Duplicate readings agreed within ±25 °C and their average indicated a temperature of 700 °C. This value compares favorably with that obtained when the brightness of the filament was matched with that of the image of the glowing spot as seen in the telescope.

Several days later it was found possible to work near the foot of the slope down which the hot avalanches were hurtling. This is a somewhat precarious occupation, but after several hours' observation it was decided that it would be feasible to measure the temperature of the extruded rocks with the portable potentiometer and Chromel-Alumel thermoelement. During one of the eruptions a mass roughly

50 feet in diameter was ejected by the volcano, broke into several pieces, and came to rest within a safe distance of our point of observation. A few minutes later the thermoelement junction, covered with a "Pyrex" tube closed at one end, was placed on one of the hot boulders (about 4 feet in diameter); a smaller rock from the original mass was lifted by two men equipped with long-handled shovels and was placed on the thermoelement. Smaller hot rock fragments were placed around the capping rock so as to afford as good a thermal insulation as possible. Maximum temperature was recorded on the potentiometer in about 30 minutes and persisted for about an hour. The reading was, as usual, corrected for the temperature of the cold junction and found to be 690 °C ± 10°, which, all considered, is a fair check on the value determined with the optical pyrometer.

Quite frequently during the extrusion of hot fragmental lava the area of eruption is covered by dust clouds; and even though the glow of the lava can be seen, there is always doubt as to the amount of correction that should be applied to the temperature readings on account of the absorption of light by the dust. It is fortunate that at Santiaguito the amount of fine particles developed at the time of extrusion is small; this is due in part to the matrix of hot, pasty material that entraps the lava and in part to the absence of violently explosive phenomena. It is also fortunate that the areas of extrusion begin to glow several minutes before extrusion actually takes place; during this period the air is usually free from dust. Finally, the fact that there was no great divergence between the values obtained with the optical pyrometer and those obtained with the portable potentiometer also indicates that the influence of any dust particles that may have been in the air was negligible.

This apparently low temperature may surprise the reader who usually thinks of the temperature of an extruding lava as that of the proverbial "fiery furnace." Investigations in the laboratory have shown, however, that in the presence of volatile constituents such as water the temperature at which rocks can soften may be as low as the 725 °C found at Santiaguito. Such material is usually extremely viscous, and considerable pressure is needed to make it flow: this condition is never absent during the volcanic activity of Santiaguito.

Much higher temperatures have been observed at other volcanoes. At Kilauea, for instance, measurements have been made by Daly [18] and by Day and Shepherd [19] with an optical pyrometer, and by Perret and Shepherd [20] with a thermoelement. The opportunities for making such investigations are probably more favorable at Kilauea than in any other locality. When the volcano is active, a rather free-flowing basaltic lava flows into a depression and forms a lake. This condition at times lasts for months. The size and high temperature of the lake do not permit ready access; but in spite of the difficulties encountered, Perret and Shepherd succeded, after heartbreaking attempts, in inserting an adequately insulated and mechanically protected thermoelement into the lava lake. The reading corrected for the so-called cold junction * was 1050 °C. This was truly a heroic effort and their account of the adventure makes fascinating reading. It was easily seen, however, that the thermoelement was poorly adapted for such work. For instance, the metal casing of the thermoelement was quickly destroyed shortly after the reading was made. At the temperature prevailing in the lava, sulfur combines rapidly with the iron and lowers the melting point of the iron by several hundred degrees. Attempts have been made at times to determine the temperature of lavas by inserting various metals of known melting point, but the observation just referred to shows that such a procedure must yield erroneous results.

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* The cold junction was cooled with water which boiled when the determination was made.

When the molten lava at Kilauea is actively moving, the surface often remains bright for a long time and permits the use of an optical pyrometer of the disappearing filament type. Day and Shepherd[19] used such an instrument and were able to make temperature readings during a period of two months. They observed that over a period of 23 days the temperature varied from 1070 to 1185 °C. Such a marked difference in the relatively large body of lava involves a large and rapid access of heat. Jaggar[21] made the interesting observation that, at times, solidified lava is present within the body of the lake; he also could show that at a depth of 20 feet the temperature of the lava was about 100 °C lower than at the surface. This was determined by noting the behavior of a series of Seger cones that were placed in a narrow, heavy-walled, iron tube, which with the expenditure of considerable effort was lowered into the lake of lava. Important deductions have been drawn from all these observations made at Kilauea; the influence of volatile constituents in lowering the fusion of the lava and in contributing to heat at the surface has been discussed by Day.[22]

In 1938, an unusually active and persistent extrusion of a highly mobile basaltic lava from the volcano Nyamlagira situated north of Lake Kivu in Africa afforded Verhoogen[23] an exceptionally fine opportunity for making temperature measurements of the surface of the lava. He used an optical pyrometer of the disappearing-filament type and found temperatures ranging from 1030 to 1160 °C. The higher values were obtained in those areas where the lava was flowing down steep slopes and had attained an estimated velocity of about 500 meters per minute. Under such conditions the surface was constantly renewed and remained bright. The optical pyrometer could therefore be used with assurance that the values obtained represented the true heat intensity of the lava. It is a matter of considerable interest to note that the values obtained by Verhoogen at Nyamlagira are within the same range as those obtained by Day and Shepherd on a similar type of lava.

So long as we are dealing with an actively moving lava where the hot, bright surface is constantly renewed, good estimates of temperature can be made with the optical pyrometer, but it is quite a different matter when the surface becomes covered with crusts of solidified lava. Perret[24] used a Bristol pyrometer with considerable success in determining the heat intensity of the slow-moving mass of partly chilled lava of Vesuvius. The armored thermoelement was inserted in deep crevices, and fairly concordant readings were obtained after making the usual correction for the cold junction. The temperature of the lava was found to be between 1015 and 1040 °C. If the entire mass were at this temperature it should certainly show color at night, but the surface of such slowly moving masses is at a much lower temperature than the interior and may actually appear to be black. Color can frequently be seen where ephemeral cracks appear in the surface. In this type of lava, measurements of temperature, for the present, at least, must be made with some form of thermoelectric pyrometer.

Temperature measurements obtained during a period of intense volcanic activity cannot claim the same degree of accuracy as those secured at hot springs and fumaroles, but those given in this paper for the particular type of extrusion mentioned do give a useful indication of the range of temperatures within which the emission of hot solids takes place.

Discussion

Robert B. Sosman: Zies' observations of lava extruded at temperatures between 550 and 700 °C fit in well with my estimate of the temperature of intrusion of a peridotite dike in southwestern Pennsylvania, about 450 to 520 °C. Its temperature was deduced from the effects that it had produced on fragments of included coke from a coal seam penetrated by the dike. [*Am. J. Sci.*, **35A**, 353-359 (1938)].

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Upper-Air Temperatures Obtained by Use of Radiosonde

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This article is a brief description of the methods used to obtain temperature measurements of the upper air, especially with radiosondes. The term "upper air," as used here, applies to the lower levels of the atmosphere extending from the surface to a height of about 25 kilometers, which is about the maximum height attainable with the equipment now used. A "radiosonde," formerly called "radio-meteorograph," is a light instrument, carried aloft by a free balloon, and transmitting radio signals which can be interpreted in numerical values of pressure, temperature and humidity.

Temperature measurements aloft by means of free balloons carrying suitable recording instruments have been made from time to time for over forty years. But the data from these observations were not available until considerable time had elapsed—sometimes months—when the instruments were found and returned to the meteorologist. While the information so obtained had only general scientific value, it proved so interesting that daily observations were desired in order that they might be used in conjunction with other synoptic data for forecasting purposes. To this end, airplanes were used. Daily recordings were made to heights between four and five kilometers using a recording (non-radio) instrument fastened under a wing. Soundings were made daily at about 25 stations until the radiosonde took their place.

The radiosonde has some advantages over the airplane:

(1) It can reach greater heights, including the stratosphere.
(2) Data are obtained more promptly.
(3) It can be launched in bad weather when flying is impossible, and when information is most desirable.
(4) It is relatively free from danger of personal injury, especially since helium is now used for balloon filling, and since, after the balloon bursts, the radiosonde drops slowly by means of a parachute.

Development of this instrument began about twenty years ago, but progress was very slow, and it has been only about five years since satisfactory soundings could be made. However, their extensive use would have been limited by the high cost of each observation. Development and use of the radiosonde was accelerated when a process was devised to manufacture balloons at a price about one-tenth that formerly paid, thus making the cost of an observation comparable with that of an airplane observation.

Since there is extensive literature describing various types of radiosondes and their operation, a detailed description will be omitted in this paper. Suffice it to say that they are divided into two classes: the Olland system and the Modulated system.

In the Olland system, a clockwork or small electric motor rotates an arm over a set of contacts much like the distributor in an automobile ignition system, so that when a contact is established, a radio signal is emitted for the duration of the contact. Some of these contacts are fixed and others are at the end of their respective sensitive elements, and hence movable. The time interval between fixed contacts establishes the cycle, or measuring scale, and the varying intervals of time between the fixed and movable contacts are a measure of the deflection of the elements under consideration.

Fig. 1 is a photograph of an Olland Instrument of the "Galcit" type. The bimetal thermometer is directly connected to an arm bearing contact C, whose position depends upon temperature. On the lower side of the base plate is a clock revolving arm A, which closes an electric circuit whenever it touches either movable contacts C and B or fixed contacts D and D^1. The radio transmitter, not shown in the picture, emits a radio signal for the duration of a contact. On the ground a radio receiver operates a relay leaving a mark on a paper which is fed at a uniform rate. Temperature is then indicated by the ratio of distances measured on the paper, or time intervals between contacts, and is equal to D^1C/D^1D. Before the instrument is launched, a calibration is made in the laboratory establishing relationship between temperature and the ratio of time intervals.

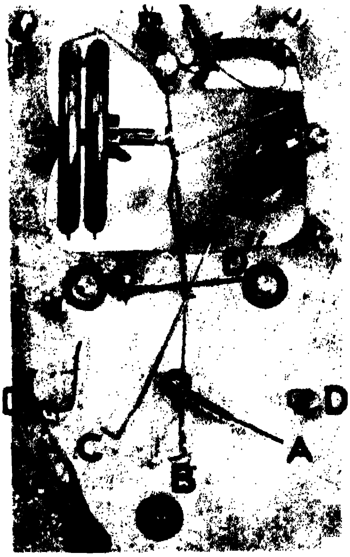
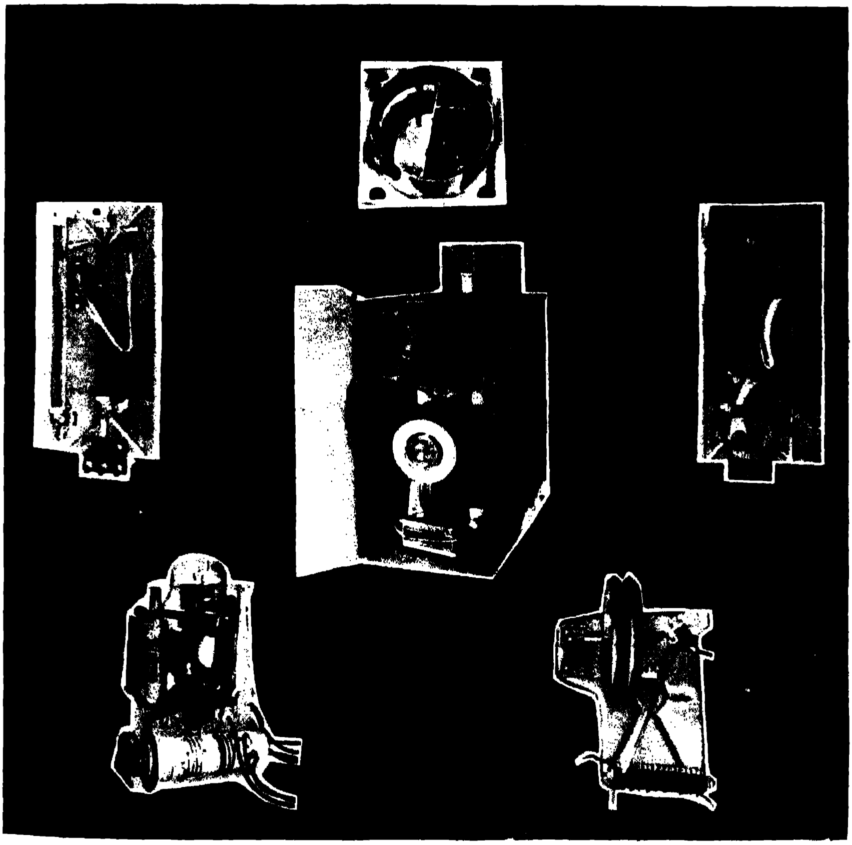


Fig. 1.

In the Modulated type there are two methods of transmitting radio signals: one method has each of the various elements, that is, pressure, temperature, and relative humidity, control a condenser whose capacity controls the radio frequency. A contact device, similar to the one described for the Olland system, closes a number of circuits in sequence, each of which is in a different radio frequency band. The receiver is tuned to cover all bands, and the indicators of the dial (now made to be automatically recording) are a measure of the frequency emitted, which, in turn, is a measure of the deflection of an element. The other, now in use in the United States, is one in which the radio frequency is kept constant but is interrupted at such a rate as to give an audio frequency note in the receiver. The modulation of the carrier wave is done by a special audio oscillator whose frequency is a function of the resistance in the circuit. In this case, the measuring elements must show changes in the resistance of that circuit.

In all the instruments mentioned, with the exception of the Modulated audio frequency system, the temperature element consists of a bimetallic strip whose deflection with changes in temperature is made known, in the case of recording instruments, by the position of the stylus on a smoked surface, and in the case of radiosondes, by methods just indicated. Needless to say, in all cases, the bimetal is mounted so that it is least affected by heat conduction through its support, and is equipped with a highly polished air duct to protect it from radiation. However, with the modulated audio frequency system, there is a radical departure. Here the thermometer consists of a fine capillary tube filled with electrolyte. The tube has a "V" shape for maximum ventilation, and its ends terminate in bulbs to provide for expansion of the electrolyte and room for the electrodes. The electrolyte shows a large change of resistance with changes of temperature. In the radiosonde, this temperature tube connected to the special audio oscillator circuit provides the resistance whose magnitude controls the frequency of modulation. The temperature of a received signal is determined from a known relation between modulated frequency and resistance, and between resistance and temperature.



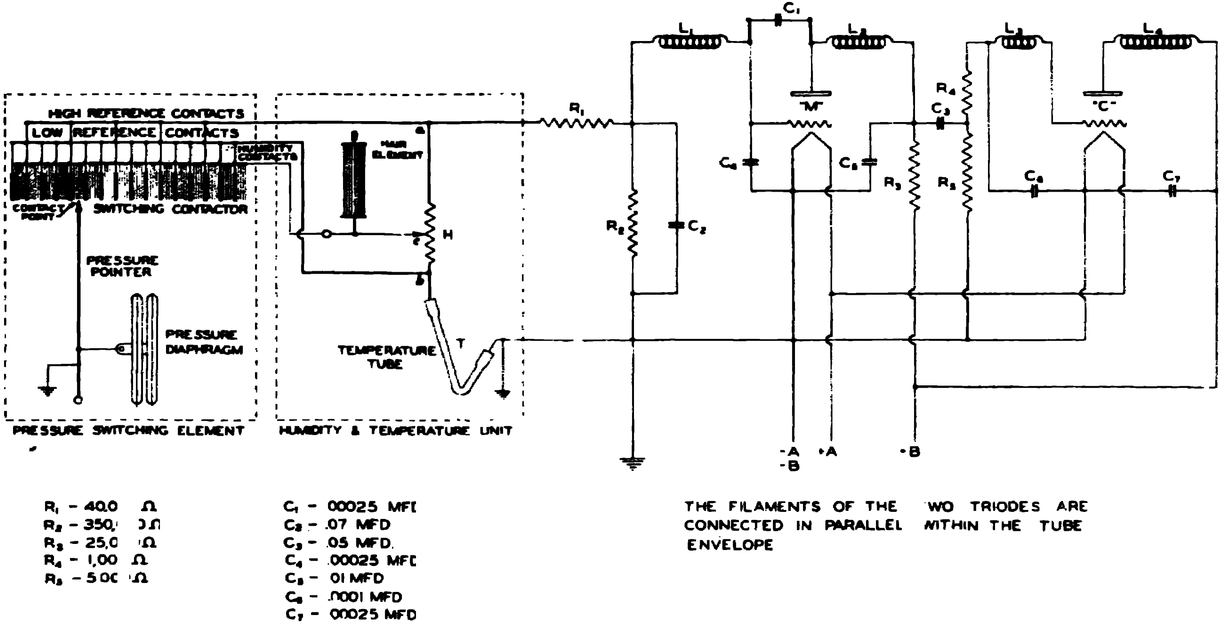
Courtesy National Bureau of Standards.

Fig. 2 shows a radiosonde of the audio frequency modulation type (Diamond-

Hinman System) with the cover opened. Around it are shown the parts comprising the instrument. *A* is the ventilation tube in which are placed the temperature and humidity elements, exposing them to maximum ventilation with a minimum amount of radiation and conduction effects. The capillary tube, forming the temperature element, and the hair hygrometer, are mounted on plate *B*. *B* shows the opposite side of the plate and indicates how a change of length of the hair causes a change of electrical resistance by means of a cam and a wire wound resistor. *C* is the radio transmitter and relaxation oscillator combined. *D* is the pressure element, and serves the dual purpose of indicating pressure as well as alternately switching the temperature and humidity elements in the oscillator circuit.

A pressure change will cause the contact arm to move along the switching contactor. When over an insulator section, the temperature tube is in the circuit, when contact is made with a metallic section, the humidity resistor is in the circuit. For a range of temperature of about 130 degrees C (40 – 90 °C) the oscillator operates from about 140 to 12 cycles per second. The range for relative humidity is from 160 to about 190 cycles per second. Barometric pressure is indicated whenever contact is made with a metallic section. Before use, each radiosonde has the pressure element calibrated in the laboratory to establish a relationship between pressure and the number of a metallic section. Fig. 3 is a schematic diagram of the radio and audio oscillator circuit, and the meteorological elements. As will be noted, a number of the metallic sections are not in the humidity circuit, but some are connected to the low end of the humidity resistor, and others to the high end. Low reference contacts will give a constant frequency which serves as a base for measuring temperature and humidity frequencies. High reference contacts establish the highest frequency. The two reference frequencies establish index points on the barometric as well as humidity scales.

When airplanes were used for making soundings, the recording (non-radio) instrument was used day after day and was recalibrated only at occasional intervals. This calibrating, though elaborate and taking considerable time, was not a severe handicap because it was applicable to a large number of soundings. With free balloon instruments there should be just as complete a calibration for each sounding. Since the same accuracies are desired, even greater refinements must be observed, for in this case, measurements are made over a greater range. They also require more careful handling because, being made as light as possible and intended to be used only once, or at the most, several times, they could not have the same workmanship and strength as the airplane meteorographs. In order that radiosondes may be practical for routine use, calibrations must be made rapidly at low cost without loss of accuracy. Calibration methods with the bimetal thermometer vary from immersion in liquid baths at different temperatures to the following procedure: both the temperature and pressure elements are made to undergo changes in a special chamber at such a rate as to simulate the changes encountered during a sounding. It is apparent that it would be impractical to use radiosondes in which there must be a complete temperature calibration for each instrument. It is thought it would be possible for bimetals to be manufactured, and if properly treated and adjusted, make them so nearly identical (within a fraction of 1 °C) that they may be used without calibration, or at most a partial one, and only occasional checks made on random instruments to assure constant quality. This has not been done so far, but it is expected that several manufacturers may introduce this method, thus making radiosondes using bimetal thermometers as convenient for use as the modulated audio frequency type. In the latter case, temperature indications depend only on the resistance of the electrolyte, and calibration accuracy will be constantly maintained as long as the temperature resistivity coefficient of the electrolyte


HIGH REFERENCE CONTACTS
LOW
REFERENCE CONTACTS
HUMIDITY CONTACTS
CONTACT POINT
SWITCHING CONTACTOR
PRESSURE POINTER
PRESSURE DIAPHRAGM
PRESSURE SWITCHING ELEMENT
HAIR ELEMENT
a
c
b
H
T
TEMPERATURE TUBE
HUMIDITY & TEMPERATURE UNIT
R1
R2
C2
L1
C1
L2
"M"
C4
C5
R3
C3
R4
R5
L3
"C"
L4
C6
C7
-A
-B
+A
+B
R1 - 40,0 Ω
R2 - 350, Ω
R3 - 25,0 Ω
R4 - 1,00 Ω
R5 - 500 Ω
C1 - 00025 MFD
C2 - .07 MFD
C3 - .05 MFD.
C4 - .00025 MFD
C5 - .01 MFD
C6 - .0001 MFD
C7 - .00025 MFD
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remains constant. This condition can be satisfied whenever the electrolyte solution is made up. There is one more condition, namely, that the audio oscillator circuit shall have identical characteristics in all radiosondes. Fortunately this is attainable in manufacture, and in addition the characteristic is both easily and quickly checked. The present requirement is that this radiosonde shall agree in its indications with those of a standard thermometer within $\frac{3}{4}$ °C. The Weather Bureau is now using the audio frequency modulated type of radiosonde at all its stations without an individual temperature calibration for each instrument, dependence being placed on a constant electrolyte and oscillator circuit. There are, of course, occasional comparative soundings made simultaneously with recording instruments in order that we may be satisfied nothing is wrong. Agreement between the two types has been within the readability of instruments.

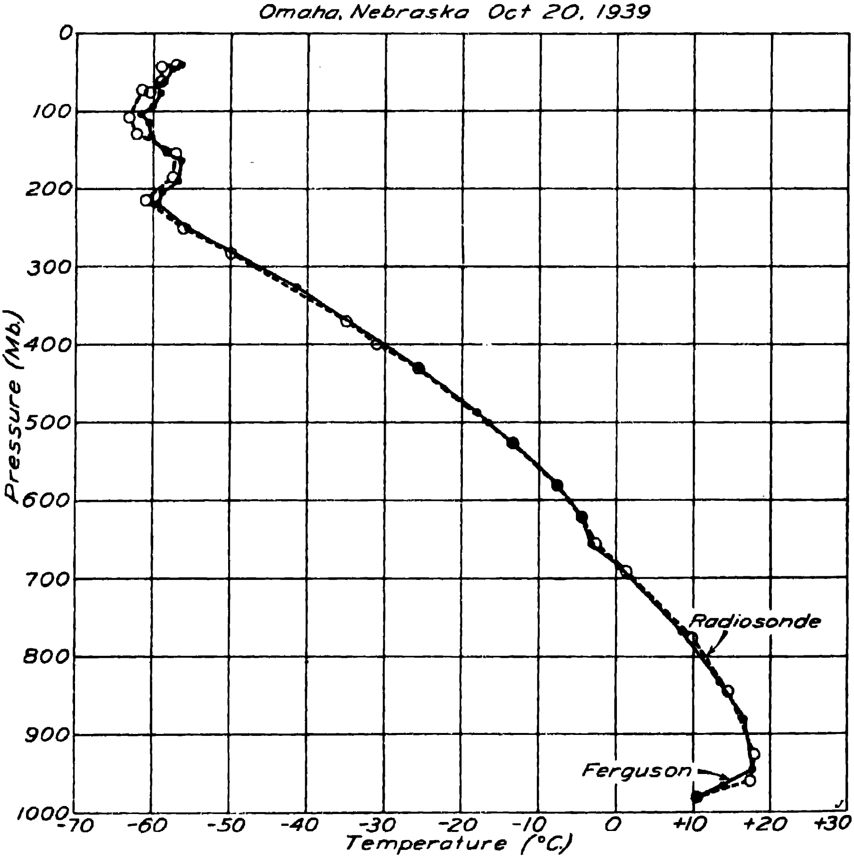

FIG. 4.

The comparison recording instrument, known as "The Fergusson meteorograph," is a combined barograph-thermograph and hygrograph, whose elements consist of a bimetallic thermometer, a bourdon pressure cell and a hair hygrometer. Each operates a stylus which leaves a trace on the smoked surface of a cylinder revolved by a light clock. There is also a fixed stylus which marks a reference line from which measurements are made to the other traces for evaluating the record. The completed instrument weighs about 250 grams and is well suited for balloon soundings. However, its usefulness is limited by its high cost, and, what is worse, one must wait until the instrument is found and returned. The airplane instrument, formerly used for daily soundings, is quite similar, but is larger, heavier and more rugged.

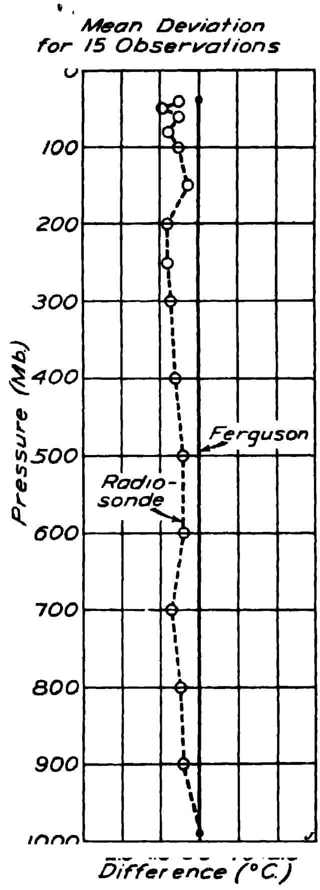

FIG. 5.

In October, 1939, a series of comparative recordings was made by the Weather Bureau at Omaha, Nebraska. This location was selected because it has been most favorable for the recovery of recording (non-radio) instruments which drop to earth in parachutes after the balloon has burst. Fig. 4 is a diagram of the radiosonde observation made on October 20, 1939 on which is plotted for comparison the record from the Fergusson instrument. Fig. 5 is a diagram showing the mean difference between radiosondes and recording instruments at various pressure levels.

A factor which is not known quantitatively is the sensitivity or rate of response to temperature changes. Because of lack of apparatus, no precise tests have been made. Only by comparing results with different instruments and different ascensional rates are we satisfied that no appreciable errors exist from thermometer lag. Similar results are indicated when readings are compared with a small thermocouple during temperature changes at a rate approximating the temperature changes of an ascent.

A serious difficulty is encountered when temperature measurements are made at upper levels. Hitherto, in all temperature measurements, we depended upon the thermometer to acquire the temperature of its surroundings by means of heat transfer through thermal conduction to the air flowing past it. When measurements are made in rarefied air, this is no longer the major process of heat exchange; radiation enters the picture. Thus we may expect that the material, texture, and color of a thermometer may affect its indications. Since soundings are most made at night, a serious source of error due to solar heating is eliminated. As far as night soundings are concerned, a comparison of the results obtained from different types of instruments show that their temperature indications are reliable up to the heights usually obtained. There have been no extensive soundings with the radiosonde in daytime thus far, and it is not known how temperature indications aloft would be affected.

Based on data obtained from recording instruments, there is strong evidence that there is a diurnal change of temperature in the upper atmosphere (above 14 kms) not found in layers immediately below it. A program of frequent daily soundings at different times of the year is necessary to determine the magnitude of these changes. There are also other changes indicated which may be due to atmospheric processes not as yet determined. For instance, in making a number of soundings in the vicinity of a hurricane, the temperature in the stratosphere has shown a marked increase. This has been recently confirmed by a few radiosonde observations.

The radiosonde is now in regular use for daily observations, and is proving so successful that it will doubtless continue in use. Furthermore, the heights attainable being much greater than with airplanes, a great deal of information is being obtained which, when studied, will provide us with a fuller knowledge of the atmosphere and its behavior.

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Upper-Air Temperatures and Their Significance in Air-Mass Analysis

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The greatest progress in meteorology and its application to forecasting is now being made by substituting a three-dimensional for the former two-dimensional day-to-day picturization of the atmosphere. This third dimension is being furnished by upper-air observations. As long as no system of upper-air observations existed, no very clear picture of the structure and dynamics of the air masses could be obtained, and forecasting had to be developed on the basis of correlating certain types of sea-level pressure distribution and pressure change with subsequent weather. In the hands of a few keenly observant men, empirical forecasting by this technique in the early part of this century attained an appreciable degree of success; but it has definite limitations.

These largely empirical methods were followed by the first stage in our progress toward the complete utilization of the third dimension in weather analysis and forecasting, namely that of "indirect aerology." By making use of a few individual kite and balloon ascents, meteorologists found that certain types of vertical distribution of temperature and humidity characterize certain happenings in the weather. Most important of all, a three-dimensional view of the extratropical cyclone was obtained by means of occasional series of soundings at single stations, showing the existence aloft of different air masses and of fronts, which were found to be sloping surfaces of discontinuity separating the air masses. Certain types of cloud forms or time sequences of clouds, types of precipitation, visibility and wind conditions were found to be associated with specific types of vertical atmospheric structure. Thus, without the aid of a network of sounding stations, "indirect aerology" could be applied by observing from the ground the phenomena just mentioned in order to obtain a rough picture of the atmosphere in three dimensions. Out of these painstaking efforts, practical methods for the intensive daily application of air-mass analysis to weather analysis and to forecasting were developed by a group of Norwegian and Swedish meteorologists.

We have now entered the period of *direct aerology*, which makes it possible for us to obtain a true, instantaneous picture of atmospheric structure by means of a network of upper-air sounding stations taking simultaneous observations and covering a large area. In the United States we have had in operation during the past 5 years first a network of nearly 30 airplane sounding stations, where military planes and small commercial planes under Weather Bureau contract simultaneously made daily flights with recording instruments, and more recently a similar network of radiosonde stations.

The most obvious method of representing the upper-air structure is by means of vertical cross-sections in varying directions between the stations. With the present network it is possible to obtain daily cross-sections in many different directions through the atmosphere. One of these cross-sections is shown in detail in Fig. 1b, corresponding to the weather map of Fig. 1a. Since the general circulation of the atmosphere in our latitudes is from west to east, we in the eastern part of the country are able to obtain an excellent picture of the region of the atmosphere that is approaching us. On the Pacific Coast the forecaster is not so fortunate and must still rely on indirect aerology. This is also true in analyzing weather conditions in the northern Canadian region. In Western Europe the forecasters, like ours on the Pacific Coast, must rely on indirect aerology. We hope that the rodiosonde instrument will bring these regions into the domain of direct aerology; and in looking to the future we anticipate radiosondes from aboard ships at sea, which will open up an entirely new field of upper-air exploration. With the development of transoceanic airplane travel, the demand for more ocean weather information should give us further justification for soundings into these little-known regions.

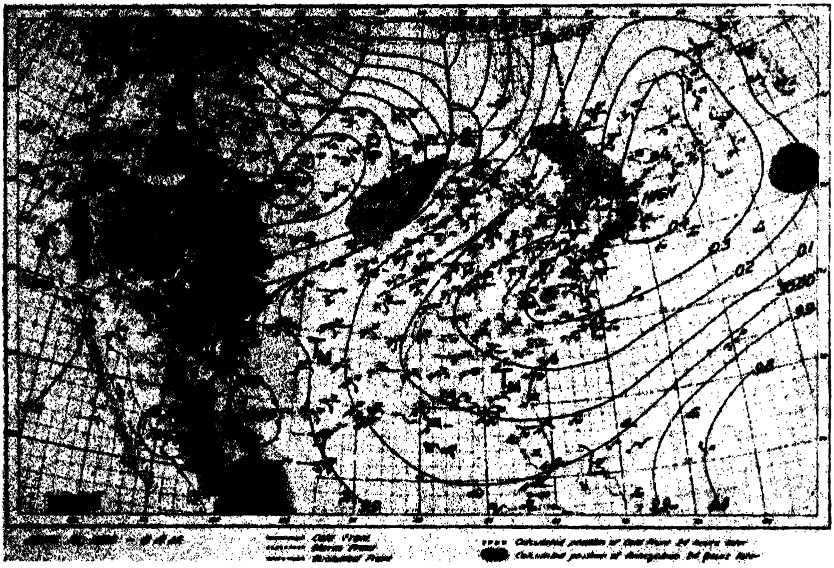

FIG. 1a. Analyzed weather map, showing fronts and air masses.

The adiabatic chart (Fig. 2) is the fundamental diagram for plotting the data from individual ascents. The sounding is plotted with temperature as abscissa, and pressure on a logarithmic or exponential scale as ordinate which is approximately equivalent to a linear altitude scale. On the diagram, we may readily locate the various temperature inversions (atmospheric strata in which the temperature increases instead of decreases with height) which are significant as marking the tops of turbulent and convectively-stirred regions and which also coincide with the tops of haze, smoke, and cloud layers. Furthermore, these temperature inversions, especially if accompanied by inversions in the vertical distribution of moisture, may signify the presence of frontal surfaces. Adaptations of the adiabatic chart have been devised, from which the energy realizable for vertical convection can be determined—one of the few precise physical computations that can readily be applied to forecasting, and which is of great value in forecasting local showers and thunderstorms. The procedure consists in following the changes that would occur were an isolated element of surface air forced to move upward along an adiabatic line, and comparing its temperature, and therefore its density, at each level with that of the surrounding atmosphere through which the element is forced to rise;

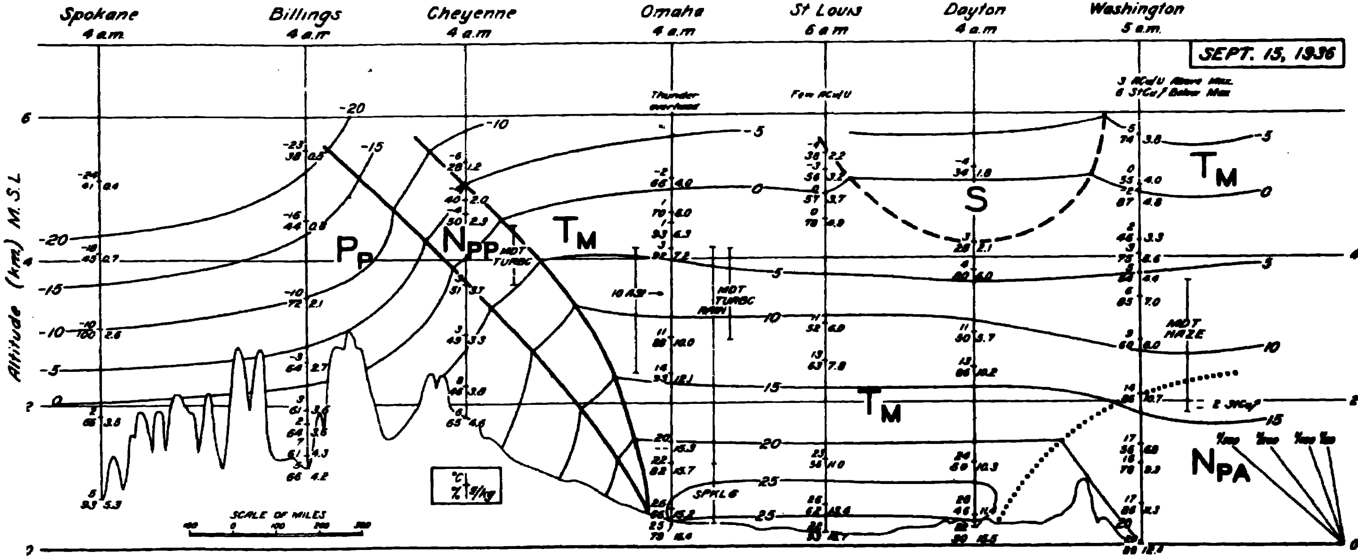

FIG. C ough atmosph ponding Fig.

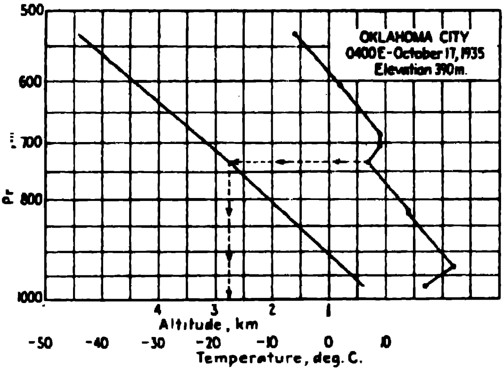

FIG. 2. Adiabatic chart.

the conditions in the surrounding medium are given by the data of the upper-air observation. If the isolated rising air finds itself in an environment that has a lower temperature, then it will not be in stable equilibrium and will be accelerated upward, thus being capable of producing the strong ascending currents necessary for the formation of thunderstorms. In its ascent, the air, after reaching the con-

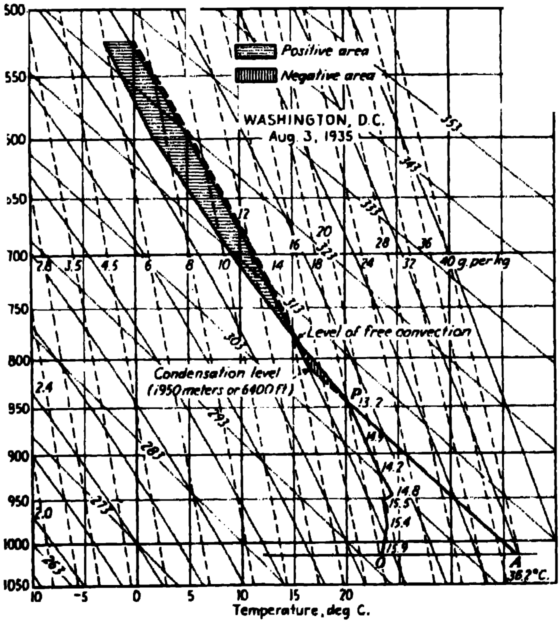

FIG. 3. Emagram.

densation level of its water vapor, cools at the so-called saturation—or pseudo-adiabatic-rate, which is less rapid than the adiabatic cooling rate before condensation because of the gradual release of the latent heat of vaporization in the cloud. A convective-energy diagram called an "emagram," based on the adiabatic chart, is shown in Fig. 3; it can be shown that the so-called "positive area" on the diagram is a measure of the energy available for convection.

One of the most recent and most promising advances in charting the upper air is the development of the so-called isentropic charts. This method is based on the fact that in the free atmosphere, most movements are along adiabatic or isentropic surfaces, *i.e.*, surfaces of constant potential temperature; potential temperature is defined as the temperature attained in an adiabatic reduction of pressure to 1000 millibars (one million dynes per sq. cm.). The equation for this type of reduction is such that the reduced temperature (potential temperature) is much higher than the actual temperature. The potential temperature always increases with elevation in the atmosphere, except possibly in very restricted layers. As we proceed northward or into any cold region we find that a given potential temperature occurs at higher and higher levels. Thus, a surface of constant potential temperature or isentropic surface is a sloping surface.

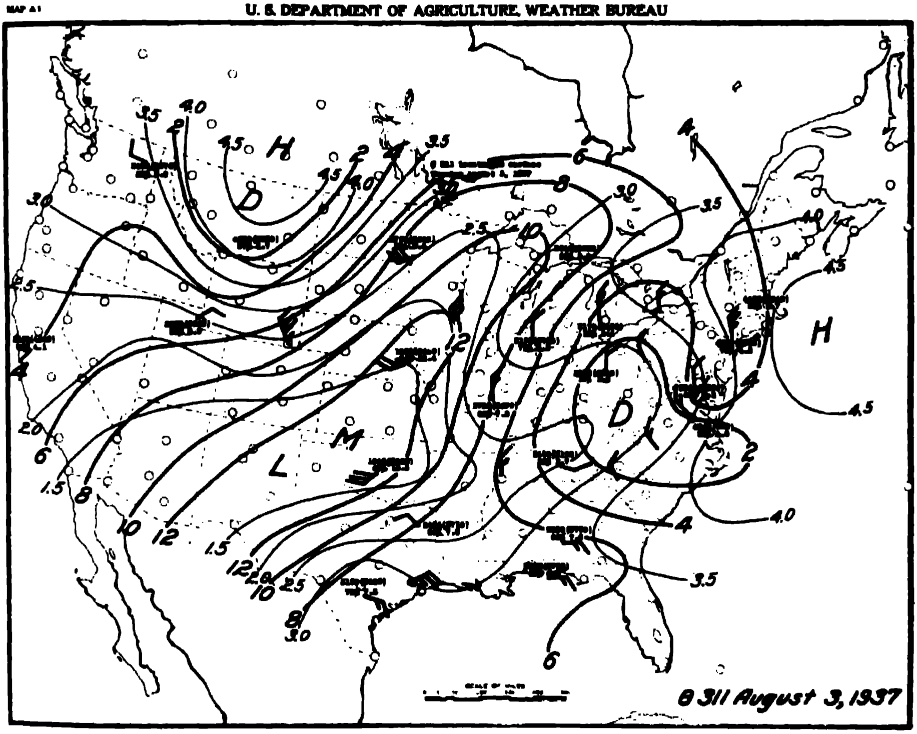

Fig. 4. Isentropic chart.

By using a network of upper-air sounding stations covering a large area, such as we have in the United States, a contour map of an isentropic surface over the United States can be constructed. The meteorological significance of isentropic charts is based on the tendency for the air to flow along isentropic surfaces, *i.e.*, moving generally horizontally, but subjected to compressional heating or expansional cooling where vertical components are present. The nature of the flow along an isentropic surface can be recognized by noting the path followed by regions of maximum or minimum water-vapor content. (See Fig. 4.) These moist tongues, especially where they are carried in currents moving rapidly upward along the isentropic slope, are correlated with areas of precipitation and cloudiness. In forecasting the behavior of these tongues, one can arrive at a very good idea of the future course or development of precipitation areas. A study of these charts has shown that the atmospheric circulation tends to break up into much smaller eddies than was previously supposed to be the case. New theories of the general circulation of the atmosphere are being developed from these findings.

What new developments will come from a network of radiosonde observations extending into the stratosphere, and taken under adverse as well as favorable weather conditions, can only be conjectured. We are especially eager to learn more about the relations between temperature and elevation of the stratosphere and weather conditions at the surface of the earth. From isolated observations we have been led to suspect that many centers of low pressure owe their development or continuance to peculiar conditions in the stratosphere. With a complete network of stations we could watch these stratosphere developments in detail and perhaps use them with effectiveness in weather forecasting.

Stellar Temperatures

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1. Introduction

The temperatures found in astronomical literature may be classed into two main groups, referring respectively to (1) the observable surfaces of the stars and planets, and (2) the interiors of these bodies. The first group depends directly on observations, although some well-established theoretical results are usually needed in the reductions; the second group depends entirely upon theoretical deductions, with observed values for the boundary, in order to make the problem defined. In addition we have temperature determinations of the highly diluted material filling the large spaces between the stars. These temperatures depend on observations interpreted with the aid of atomic physics. The total range of temperatures thus covered runs from about 3° absolute to about 50,000,000°. The lower limit is well exceeded by that obtainable in the physical laboratory; but the upper limit is reserved for the domain of astronomy, as are the upper limits of pressure and density found in astronomical bodies. The reason is that all three limits can be reached or approached only as a result of the action of gravity on large compressible masses.

Although the high pressures and densities found in the interiors of some of the stars can in no way be duplicated in the laboratory, some aspects of the high temperatures (the high kinetic energy of the particles) can now be covered by the fast particles produced in the study of nuclear processes. The energy generation in the stars, which is a result of the high temperatures and densities prevailing near the center, is therefore accessible to physical interpretation. The progress made in interpreting this process of energy generation may in turn be considered to provide a general confirmation of the temperatures computed for the interiors, on which the energy generation appears to depend in a very sensitive manner.

2. Surface Temperatures of the Stars

Obviously it is not possible to measure the surface temperatures of the stars by contact methods; but two other methods are applicable, depending respectively (1) on the laws of radiation, and (2) on the laws of ionization, in combination with those of atomic physics.

The observed spectral-energy curve, corrected for absorption in our atmosphere, provides the empirical data for both methods. The first method deals largely with the "continuous spectrum," *i.e.*, the intensity distribution of the smoothly-varying background in the spectrum on which absorption and emission lines appear. The second method deals with the total intensities (or profiles, if high dispersion can be used) of these absorption and emission lines.

The empirical data are restricted to the wave-length interval of about 2900 to 140,000 A, the absorption in our atmosphere being practically complete outside these limits. The lower absorption limit is caused by the ozone in our atmosphere. From about 3000 to 25,000 A the atmosphere is comparatively transparent, although several heavy absorption bands due to water vapor and carbon dioxide occur in the near infrared. These absorptions become even heavier between 25,000 and 80,000 A (2.5 and 8 microns). Finally from 8 to 14 microns our atmosphere is comparatively transparent, at least if it is dry. The long-wave cut-off at 14 microns is due to carbon dioxide. The transmission curve of the atmosphere for the Mount Wilson Observatory, published in 1930 by Pettit and Nicholson,[1] is reproduced in Fig. 1. It was computed for 0.7 cm of precipitable water. Since that time many new details of the transmission curve, and their identifications, have been published by Adel.[2] As is well known, much of the earlier work on the transmission of the atmosphere is due to Langley, Abbot, and Fowle of the Smithsonian Institution; Fig. 1 is largely based on their work.

3. Stellar Temperatures Derived from the Continuous Spectrum

The continuous spectrum has so far been the more important of the two sources of information on stellar temperatures. With the transmission curve of our atmosphere known (Fig. 1) it is possible to reduce the observed energy curves of the Sun and the brightest stars to true energy curves (as they would be observed outside our atmosphere). It now appears that these energy curves roughly, but not exactly, correspond to those due to blackbodies, *i.e.*, to Planck curves. We must distinguish now between two cases: (1) the diameter of the star is known (as for the Sun); (2) the diameter is not known. In the first case the ordinates of the energy curve may be reduced to absolute units (ergs emitted per cm^2 per sec); but in the second case the ordinates are only relative. In the latter case, therefore, in fitting a Planck curve to the observed energy curve, only the *shape* can be used; and if the wave-length interval is rather small, only the *slope*. Nevertheless, we shall find only one value of the temperature giving the best fit, because the slope varies in a monotonic way with temperature. This temperature is called *color temperature*.* If the star should radiate like a blackbody, this color temperature (T_c) would be the true temperature of the emitting layer. Actually, deviations from a Planck curve always appear if the wave-length interval covered is large. This shows that T_c will depend on the wave-length used, and has no fundamental significance. Its significance is purely a practical one for T_c is easily determined empirically for a great number of stars. After it has once been determined for a few bright standard stars, further determinations can be made relative to these

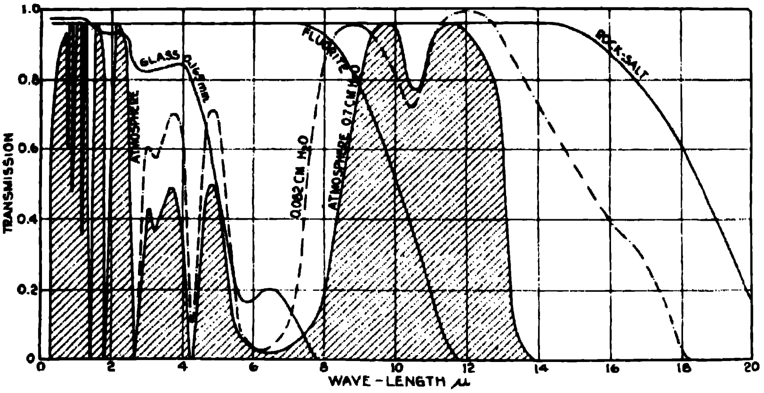

FIG. 1. Transmission curves of (a) the atmosphere above Mount Wilson (shaded curve); (b) water vapor, 0.082 cm precipitable water; (c) microscope cover glass, 0.165 mm thick; (d) fluorite, 4 mm; and (e) rock salt, 2 mm.

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* The astronomical usage agrees here with that recommended in the glossary of the Temperature Symposium.

standards by making observations at the same zenith distance, since the atmospheric absorption is the same at corresponding wave-lengths for the stars compared, and is therefore eliminated in the ratio of the energies. If these spectrophotometric comparisons are made photographically, with large telescopes, color temperatures may thus be determined for stars 10,000 times fainter than the faintest stars visible with the naked eye. We shall later mention some cases where this technic is of special interest.

More progress can be made if the diameter of the star is known. We saw that then the ordinates of the energy curve may be expressed in ergs/cm^2 sec. We can still derive the color temperature, as before, but in addition the *total* amount of radiant energy leaving the star per cm^2 per sec may be found by integration over the energy curve. This total flux is obviously a fundamental quantity. We may express it in terms of temperature by means of Stefan's law. In astronomy this temperature is called the *effective temperature*,* abbreviated T_e. It is a precisely defined quantity, of great importance for the equilibrium of the stellar atmosphere, and related to the total luminosity, L, by the relation:

$$L = 4\pi R^2 \cdot \sigma T^4_e \tag{1}$$

(R is the stellar radius, σ the radiation constant).

The aim of stellar temperature determinations is the evaluation of T_e for as many stars as possible. The color temperatures, T_c, are derived only as an intermediary step, simply because they are more easily determined for a great number of stars, and are already a first approximation to effective temperatures. They may be reduced to effective temperatures once the relation between T_c and T_e is established by means of those stars where both can be determined empirically. There is well-founded hope, however, that in the near future this relation may be reliably determined from theoretical considerations, after the theory of the continuous absorption coefficient for the stellar atmosphere has been completed satisfactorily.

From Equation (1) it follows that T_e may be found for those stars for which both L and R are known (or for which the emission per unit surface area, $L/4\pi R^2$ may be derived). Only for the Sun are these quantities accurately known; T_e(Sun) = 5713° absolute. For three eclipsing binaries the data are still useful. Finally there are half a dozen stars for which the angular diameter could be measured interferometrically at Mount Wilson Observatory. They can be used also, since the apparent brightness gives L/D^2, if D is the unknown distance to the Sun, and the angular diameter gives R/D; hence L/R^2 is found independently of D.

These ten objects exhaust the list at present, and they would be entirely inadequate if the color temperatures were not already good approximations to the effective temperatures, so that only some adjustments remain necessary.

On the basis of the foregoing discussion it would seem natural to tabulate the T_e just derived against T_c. But there is an observational quantity even more easily determined with accuracy than T_c and closely related to it. It is the so-called *spectral type*. Originally the stars were ordered by their spectra according to the symbols A, B, . . etc.; but later several symbols were dropped as superfluous, and the order of the remaining ones, if arranged according to decreasing surface temperature, is now O, B, A, F, G, K, M, if we omit a few rare types from consideration. These types are further subdivided into 10 smaller steps: B0, B1, B2, ... B9, A0, A1, ... A9, F0, etc. Most of the stars in a volume of space belong to the sequence

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* It corresponds to the *radiation* temperature of the glossary. The astronomical usage dates back several decades.

O, B, . . . M, in which the radii of the stars progressively decrease, and also the luminosities. But the latter decrease very much faster than the former, because most of the decrease of the luminosities is due to the decrease in T_e [*cf.* Equation (1)]. These stars are said to belong to the *main sequence* (or the *dwarf* stars); the Sun is one of them. For this sequence there is practically a one to one correspondence between spectral type and T_c, and also between T_c and T_e. Hence the most practical procedure is to give T_e immediately as function of the spectral type. This is done in Table 1.

Table 1. The Stellar Temperature Scale.*

Sp.	T_e	Sp.	T_e
A0	10,700°	gG0	5,200°
A5	8,500	gG5	4,620
F0	7,500	gK0	4,230
F5	6,470	gK5	3,580
dG0	6,000	gM0	3,400
dG2	5,710	gM2	3,200
dG5	5,360	gM4	2,930
dK0	4,910	gM6	2,750
dK2	4,650	gM8	2,590
dK5	3,900		
dM2	3,200		

d = dwarf; g = giant.
Temperatures in centigrade absolute.

* For the details of the derivation, see a paper by the author, *Astrophysical J.*, **88,** 429 (1938). Table 1 of this paper corresponds to Table 13 of the paper quoted.

In addition to the main sequence (or dwarfs) there are *giant* stars which are roughly 100 times larger in diameter than the dwarfs, and have somewhat larger masses. Since the value of the surface gravity is proportional to M/R^2, it follows that the surface gravities, and consequently the pressures and densities in the atmospheres, are roughly 10^2-10^4 times lower in giants than in dwarfs. In general, the spectral type is based on the strength of the spectral lines, and is therefore a measure of the degree of ionization and excitation in the stellar atmosphere. With the greatly diminished densities in the giants, lower temperatures than those existing in the dwarfs are sufficient to produce the same degree of ionization (or the same spectral type). This difference in temperature between giants and dwarfs is considerable for types G and K, as is shown in Table 1. Certain complications arise at the ends of the spectral sequence, connected with the significance of the criteria used in the classification.

We have indicated how L/D^2 is obtained from integration over the energy curve (L=luminosity, D=distance of star to Sun). In practice it appears to be sufficient to do this for a number of standard stars of different spectral type, and then to determine which corrections should be applied to the apparent *visual* brightnesses in order to obtain the so-called apparent *bolometric* brightness, L/D^2. Such corrections are called bolometric corrections. The word *bolometric* refers in both cases to the non-selective recording of energy by the bolometer.

For the Sun the energy curve has been determined in considerable detail,[3] but for stars it is not possible to use high dispersion in the infrared, where the sensitive photographic methods cannot be used. For cool stars ($T_e < 4000°$), which have a considerable infrared intensity, the energy curve is most readily studied by means of a sensitive thermocouple placed in the focus of a large telescope. The different intervals of wave-length are then separated by means of filters.[4] With a correction for atmospheric absorption the true energy curve is at once obtained. For stars of about the solar temperature (with the maximum of the energy curve near 5000 A) either the photographic or the photoelectric method of recording energies in the spectrum is useful; but both methods need a calibration by means of a standard having a known energy distribution, before the true energy curve is found. For still higher temperatures the same two methods may be used, but for temperatures much higher than 10,000° the results become uncertain, since the maximum of the energy curve then falls below 3000 A. Fortunately for these high temperatures additional information may be obtained by the method discussed in Section 5.

4. Applications

The previous discussion indicates how the energy curve, L/D^2, T_c, and T_e are determined. We have also mentioned the importance T_e has for the interpretation of the stellar spectrum, and the mechanism of the atmosphere. But the most urgent reason for making precise T_e determinations is a different one.

The three most fundamental empirical data about a star are its mass, M, its luminosity, L, and its radius, R. It is the object of theoretical astrophysics to use these data for as many stars as possible in a study of stellar structure, stellar energy generation, and stellar evolution, which are perhaps the most fundamental astronomical problems. The determination of masses is restricted to certain suitable groups of binaries. For one of these groups (visual binaries with well-known D), L may be found, but R has to be computed from Equation (1), after T_e has been determined; whereas for the other group (eclipsing binaries) R is found in absolute units, but L can be found only by (1) from R and T_e, since D for these objects is too large for a determination from the parallax.[5]

Another application of T_e determinations is made in the study of *white-dwarf* stars. They are stars of low luminosity (dwarfish), rather high surface temperature (white), and hence, by Equation (1), of very small radius. Since the masses of these stars are roughly equal to that of the Sun, the average densities (being proportional to M/R^3) are excessively high, 10^5-10^8 times water. The matter of these objects, except for an outer fringe which is gaseous, is in the degenerate state, obeying Fermi-Dirac statistics. Here again we have conditions far outside the range obtainable in physical laboratories. Because the essential conclusions depend directly on the results of T_e determinations, the writer's recent results on eight of these objects are given in Table 2. They are the first measures of temperature made on white dwarfs (most of which are very faint), and are only approximate and somewhat provisional except for the second star, which is well determined. There is no doubt, however, that the order of magnitude is correct for all stars included.

It is necessary to point out that for white dwarfs the relation between the observed T_c and the desired T_e cannot be established empirically. Fortunately the theory of the continuous absorption coefficient is sufficiently well advanced to be useful here; it appears that with exception of a certain range of temperatures, the relation of T_c to T_e is the same as for the main sequence, where this relation is known empirically.

In Table 2 we have expressed L and R in terms of the Sun and they are fairly well established. The mean densities, depending on M/R^3, are less well known, first, because errors in R are increased more than three-fold in these values, and secondly, because M is known empirically only for the first three stars. For the remaining stars M has been computed from R by means of Chandrasekhar's theoretical relation between these two parameters. This relation involves, however,

Table 2. Surface Temperatures of White Dwarfs, and Results Derived Therefrom.

Name	T_e	L	R	Mean Density
Sirius B	9500°	0.0030	0.020	170,000
40 Eridani B	13500	.0080	.016	160,000
van Maanen 2	8200	.00016	.0062	12,000,000
AC 70°8247	35000 ±	.021	.0039	>30,000,000
Ross 627	15000 ±	.0010	.0046	>19,000,000
Wolf 489	5070	.00007	.0105	> 1,000,000
Wolf 457	10000 ±	.00011	.0034	>50,000,000
Wolf 219	15000 ±	.00052	.0033	>50,000.000

the mean molecular weight per electron, which may vary between 1 and 2, depending on the amount of hydrogen present. We have given the minimum values of the mean density, based on the extreme case in which no hydrogen is present. The other extreme, valid for pure-hydrogen stars, would give values about 4 times higher and the actual value is probably closer to the lower limit than to the upper limit. The foregoing discussions will suffice as illustrations of the importance of the temperature problem in astronomy. In the next section we mention briefly how surface temperatures ranging from 10,000 to 100,000° are determined.

5. Stellar Temperatures Derived from Spectral Lines

The strength of an absorption line in a stellar spectrum depends on a great number of factors, of which the temperature is only one: it depends on the ratio of the absorption coefficient inside the line (taken for each wave-length separately) to that just outside the line, in the continuous spectrum. This means that a theoretical prediction of the strength of a line requires the knowledge of the mechanism responsible for the continuous spectrum as well as of the concentration of atoms in the level from which the absorption takes place, the atomic transition probability, and the various effects which broaden the line (radiation damping, Doppler effect of the atoms, due to temperature motion as well as to convection currents of the gases, and pressure effects). The concentration of atoms in the level under consideration depends on the abundance of the element, the degree of ionization (which depends on temperature and surface gravity), the excitation potential of the level, and again the temperature. Since, however, in a stellar atmosphere no strict thermodynamic equilibrium obtains (since otherwise no lines would be visible!) the population of atoms in different levels is not strictly governed by the Boltzmann law. The precise allowance for this deviation from thermodynamic equilibrium is very difficult. Hence it is in general not practicable to obtain temperatures from absolute intensities of absorption lines, even apart from the difficulty caused by the uncertainty of the abundance of the element.

Several of these difficulties are avoided if the behavior of a line or a series of lines originating from the same level (as the Balmer series of hydrogen) is studied along the main sequence (O, B, A, etc.). Assume for a moment that the continuous absorption coefficient were constant along this sequence. Then the *variation* in the strength of the line (or the series) would indicate the variation of the number of atoms in the appropriate level. Now consider as an example the Balmer series, which does not originate from the ground level of hydrogen, but from the second level. For low temperatures nearly all the atoms are in the ground state and very few in the second state. For very high temperatures nearly all the atoms are ionized and again very few atoms will be in the second state. In either case the Balmer lines will be weak. But there will be an intermediate temperature at which the ionization is not yet too far advanced, but which is yet high enough to raise many of the neutral atoms to the second quantum level. Obviously this interplay of two opposing tendencies will lead to a maximum of intensity of the Balmer series at medium-high temperatures. Actually the position of the maximum will be somewhat affected if we now take into account the known variation with temperature of the continuous absorption. But the assumption of the constant abundance along the main sequence remains unavoidable. Fortunately we have evidence that most of the stars of the main sequence have roughly the same composition; furthermore, the position of the maximum is not based on one star, but on many stars, so that individual variations of abundance are mostly eliminated in the mean result. Finally we have not one, but several elements which are suitable for this analysis: H, He, N, Si, C, and O, some of them in various stages of ionization. These different elements give independent results, in which the small variations in abundance remaining in the determination of the intensity maxima enter as accidental errors. From the remarkable accord between the temperature determinations as a function of spectral type, obtained from the different elements, we conclude that the effect of variations in abundance on the temperature scale may be considered to be negligible.[6]

The resulting temperature scale is found in Table 3, taken from a paper by the writer,[7] and is largely based on computations by Pannekoek.[6]

Table 3. The Stellar Temperature Scale. Temperatures in Centigrade Absolute.

Spec.	log T_e	T_e	Spec.	log T_e	T_e
O5	4.9	80,000°	B2	4.31	20,000°
O6	4.8	63,000	B3	4.27	18,500
O7	4.7	50,000	B4	4.23	17,000
O8	4.60	40,000	B5	4.19	15,500
O9	4.50	32,000	B6	4.16	14,500
B0	4.40	25,000	B8	4.09	12,300
B1	4.36	23,000	A0	4.03	10,700

6. Planetary Temperatures

For stars we have no *a priori* knowledge of the surface temperatures. But for the planets and the Moon we are able to predict the surface temperatures with fair accuracy if we assume that the planetary heat is due entirely to absorbed solar radiation, and not partly to internal sources.

Suppose the planet absorbed and emitted as a blackbody. Then, if L is the known luminosity of the Sun, the energy received by the planet per unit area at a point where the Sun is in the zenith, is $L/4\pi D^2$, if D is the known distance of the planet from the Sun. Since by hypothesis all this energy is absorbed and reradiated, the surface temperature, T, is given by

$$L/4\pi D^2 = \sigma T^4, \text{ or } T = \left(\frac{L}{4\pi\sigma}\right)^{1/4} \frac{1}{D^{1/2}} = \frac{390\,^\circ\text{K}}{D^{1/2}} \tag{2}$$

if the numerical values of L and σ are substituted, and if D is expressed in astronomical units (distance Sun − Earth = 1).

Actually the planets and the Moon are not black; but their reflectivity can be determined from the measured brightness and the known distances of the planet from the Sun and the Earth, together with the known brightness of the Sun. These reflectivities vary from about 0.07 for the Moon and Mercury, to about 0.59 for Venus. The light that is not reflected is absorbed, and its amount is therefore also known. We may call the absorbing power A. The emissivity for planetary radiation, E, can only be estimated. Equation (2) now becomes

$$AL/4\pi D^2 = \sigma E T^4, \text{ or } T = \frac{390\,^\circ\text{K}}{D^{1/2}}\left(\frac{A}{E}\right)^{1/4} \tag{3}$$

This relation holds for a non-rotating planet, for the so-called subsolar point (the point that has the Sun in the zenith). If we take a point where the zenith distance of the Sun is Z, the amount of heat received and emitted per unit area will obviously contain the additional factor $\cos Z$, and the temperature $(\cos Z)^{1/4}$. If the planet rotates fast (so that the daily temperature variation is small) an additional factor $1/\pi$ is introduced in the amount of heat received, and $\pi^{-1/4}$ in the temperature. If the planet rotates slowly, the temperature fluctuations around this "average" will be greater, depending on the properties of the planetary atmosphere, and the speed of rotation.

The principle of determining planetary temperatures empirically is the same as that described in Section 3 for stars. At first sight the case might seem more complicated, because the radiation received from the planet consists not only of the heat radiated by the planetary surface but also of reflected sunlight. This complication disappears in practice, since the two kinds of radiation are practically entirely separated in wave-length, so that a filter may be used to distinguish between them. This separation is a result of the difference in temperature between the two sources, about 6000° and 300 °K, so that the wave-lengths of the maxima fall at about 5000 A and 100,000 A (0.5 and 10 microns) respectively. Fortunately our atmosphere is fairly transparent between 8 and 14 microns if it is sufficiently dry (Fig. 1), so that the surface temperatures of most of the planets, and of the Moon, may be measured. Only for the planets beyond Saturn does the distance to the Sun become so large ($D > 10$) that the temperatures drop below 100 °K; and for these planets the radiation of wave-length shorter than 14 microns is too weak to be measured.

For the planets Mercury, Venus, Mars, Jupiter, and Saturn, and for the Moon, temperatures have been determined empirically, chiefly at the Mount Wilson and Lowell observatories.

For Mercury (which has no atmosphere) Pettit and Nicholson[8] found about 330 °C for the subsolar point when the planet has its mean distance from the Sun. This value is only about 10-15° lower than computed theoretically for a non-rotating planet (as indicated above). Part of the difference may be due to conduction.

For Venus, Coblentz and Lampland,[9] and Menzel[10] found about 50 °C at noon. Pettit and Nicholson[11] found lower values, but at both observatories the day and night temperatures on the planet were found to be rather similar, indicating that the planet is rotating slowly. (A fast rotation is excluded on the basis of measured Doppler shifts.) The temperature found for Venus may well refer to some average layer in the atmosphere, since this atmosphere is quite opaque to visual, and even to infrared, light.

On Mars the temperature at the subsolar point is near 0 °C, and probably somewhat higher in certain dark areas. The polar caps are about −70 °C. The night at Mars is probably very cold, perhaps −60 °C. The dew point at Mars is probably about as low as the latter value, in view of the extremely small water-vapor content of the atmosphere. The existence of liquid water on the planet (for which there is no direct observational evidence) can therefore probably be excluded.

Jupiter appears to have a temperature of about −135 °C, Saturn −150 °C, and Uranus less than −185 °C. These temperatures refer to an atmospheric layer in each case. For none of the planets is there definite evidence that the measured temperatures are higher than those to be expected theoretically; hence there is no evidence of internal heat raising these temperatures.

For the Moon, Pettit and Nicholson[12] found for the subsolar point +134 °C when viewed from above, and only +85 °C if viewed horizontally. The difference is explained by the rough surface of the Moon, which allows more heat to escape vertically than horizontally. Taking into account the solar radiation lost by reflection, the theoretical temperature at the subsolar point is found to be 101 °C. The dark side of the Moon is thought to be about −150 °C, a value difficult to determine with precision because of its extreme lowness.

A series of very interesting observations was made by Pettit and Nicholson during a lunar eclipse. A point near the edge of the Moon was kept under observation for about 5 hours, during which it was first illuminated by the Sun, then passed into the shadow of the Earth, and finally emerged again. The diagram showing the temperature variation is reproduced in Fig. 2. It shows the extremely rapid cooling of the surface (from about +70 °C to −115 °C) which must be the result of a small conductivity, comparable to that of pumice or volcanic ash which, on the basis of measures of the polarization of the reflected light, had already been assumed to cover the surface of the Moon.[18]

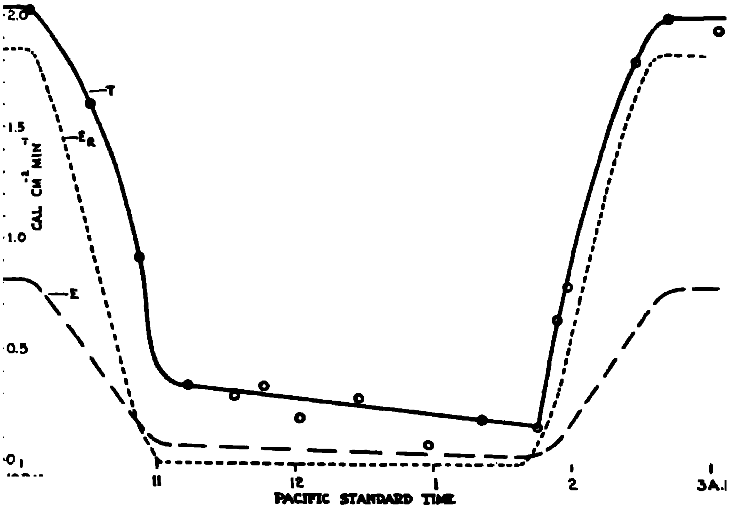

Fig. 2. March of absolute temperature, T; of energy received from the sun by the moon, E_R; and of energy radiated, E, during the total lunar eclipse of June 14, 1927.

7. Interstellar Temperatures

Although interstellar space is a far better "vacuum" than the best obtainable in the physical laboratory, it is by no means devoid of matter. The dark obscuring clouds in the Milky Way, as well as the "interstellar" absorption and emission lines prove this conclusively. These two lines of evidence point at once at the two kinds of matter occupying space. The obscuring clouds are composed of dust particles of which a good fraction have diameters between 0.1 and 1 micron; this follows from the scattering properties of these particles, and estimates that may be made of the mass of absorbing clouds. The interstellar absorption and emission lines prove the existence of gases in the atomic state. Hydrogen is by far the most abundant interstellar element, as was recently shown by Struve. Calcium, sodium, titanium, and potassium have been found from their absorption lines; oxygen and nitrogen are present in emission. Some interstellar lines are still unidentified.

The temperatures to be ascribed to the interstellar particles need some explanation. There is no more difficulty in assigning a definite temperature to a dust particle than to a planet, and it may be computed by an equation similar to (2) or (3). A particle far away from any one star would be exposed, on the average, as we are on a clear night to the starry skies except, of course, that no atmosphere would absorb the ultraviolet light, and that the stars would cover a sphere, not a hemisphere. Eddington has shown[14] that such a particle would assume a temperature of about 3 °K.

But the radiation in interstellar space is very far from being blackbody radiation corresponding to 3 °K. It contains much ultraviolet light, mainly due to the O and B stars in the sky. Hence ionization and excitation of atoms will take place in spite of the low energy density. Since the density of matter is also very low, recombinations will occur at a very slow rate. Without computations it is seen, therefore, that a fair proportion of the atoms may well be ionized. The ionizations will in turn lead to considerable velocities of the ions and electrons. Since collisions between particles are still sufficiently frequent, the velocities of the interstellar atoms, ions, and electrons will approximate Maxwellian distributions corresponding to a high temperature, roughly 10,000°, and in the proximity of hot stars even higher. Obviously there is no universal temperature of the interstellar gas; it depends on the position with respect to the stars, as the planetary temperatures depend on the distance from the Sun.[15]

8. Internal Temperatures of Stars

It can be easily shown[16] that if a star as a whole is in hydrostatic equilibrium (which is probably true for normal, constant, stars), and if the perfect-gas law holds throughout (this assumption can be verified afterwards, and found to be justified), it is possible without any further assumptions about the internal structure of a star to obtain a *minimum* value for the average internal temperature, $\overline{T}$:

$$\overline{T} > 3{,}840{,}000(\mu\beta)\,\frac{M}{R} \tag{4}$$

in which M is the mass of a star, R its radius, both expressed in terms of the Sun, μ its mean molecular weight, and β the ratio of the gas pressure to the total pressure (gas + radiation). For stars with $M < 10$ we have $\beta \cong 1$. Since the matter in a star is mostly ionized, and since the atomic weight is roughly double the atomic number except for hydrogen, we have $\mu \cong 2$ if no hydrogen is present, and $\mu = \frac{1}{2}$ if the matter is all hydrogen.

If the additional assumption is made that the stars are built on the same pattern (except for factors of scale) then the relation

$$T = C(\mu\beta)\,\frac{M}{R} \tag{5}$$

holds for corresponding points in these stars, C depending on the point selected, and on the pattern common to the stars considered.

We derive some interesting conclusions from (5). For stars on the main sequence in the neighborhood of the Sun (types A, F, G, and K), having the same hydrogen content (μ = constant), the internal temperatures will vary only slowly, because $\beta \cong 1$, as mentioned before, and M and R change in the same direction. But since M changes faster than R, the internal temperatures will increase if M increases. It is this slow increase in internal temperature which is sufficient, in connection with the high sensitivity of the energy generation on T ($\sim T^{18}$) to cause a very considerable increase of L with M (empirically $L = M^{4\frac{1}{2}}$ for the range of masses considered).

The numerical values of the internal temperatures depend on numerical integrations which cannot be discussed here.[17] We quote the values for a few stars in Table 4.

It follows from (5) that the giants (with large radii) will have low internal temperatures. This gives rise to difficulties with the explanation of the energy generation which have not yet been solved completely. On the other extreme are the massive O stars having comparatively small radius. If they were built on the same model as the less massive stars their internal temperatures would exceed 100,000,000 °C, and the energy generation would be too large by a considerable factor. Chandrasekhar has recently removed this difficulty by proposing a shell-source model for these stars, which leads to a more homogeneous density distribution than that of ordinary stars, and requires much lower temperatures for the hydrostatic equilibrium, temperatures not much higher than the minimum values required by (4), about 40,000,000 °C.

Table 4. Central Temperatures in °K.

Star	Type	T(central)
Sirius	dA1	24,500,000°
Mizar	dA2	22,000,000
Procyon	dF3	18,000,000
Sun	dG2	19,500,000
70 Oph. A	dK1	17,500,000
Capella A	gG4	5,100,000

Perhaps the highest internal temperatures occur in sub-dwarfs, stars roughly $\frac{1}{2}$ to $\frac{1}{4}$ of the diameter of the Sun, having a small hydrogen content ($\mu \cong 2$). The internal temperatures of some of these stars may well exceed 50,000,000 °C; their small hydrogen content would not lead to difficulties with the energy generation.

White dwarfs have still smaller radii, but Equation (5) is not applicable to them, because the matter is degenerate. The internal temperatures are still somewhat uncertain, but are probably at most about 20,000,000 °C.

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Chapter 5

Temperature in Biology

Temperature and Life

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The effect of temperature on all life is very obvious. We need only compare the tropics with the arctic zone, or summer with winter. The great contrasts, qualitatively as well as quantitatively, make us realize how completely life is controlled by temperature within the narrow range of not more than about 40 °C (75 °F). This range seems narrow to us because we can produce much higher or lower temperatures artificially, but the range of natural temperatures on earth above the freezing point is not much higher, and below the freezing point, life is not permanently possible, because it depends upon food grown at higher temperatures.

Because of this enormous importance. an explanation of the effect of temperature upon life has been one of the early endeavors of physiology, but not much progress could be made as long as the old conceptions of vitalism existed. Only after the life processes were considered to be exclusively, or at least essentially, an intricately interwoven texture of chemical reactions and physical processes could the effect of temperature be interpreted as the sum of all temperature influences upon each of the processes involved. Probably the first definite statement was that by Bütschli (1874) who found the metabolism of cockroaches proportional to the temperature as long as it did not interfere with the normal vitality. He concluded: "It might not be too bold to extend this direct relation to all the so-called cold-blooded animals."

In consideration of the experiments by Rhine, and more recently by several others, on extra-sensory perception, we have to admit the possibility of other factors besides chemistry and physics entering into this texture of life. Extra-sensory perception cannot be of a chemical nature since it functions over great distances, nor does it fit into any physical domains known because, among other unusual properties, it does not decrease with the square of the distance. No statement can be made about the influence of temperature upon this unknown life function, but it seems safe to assume that it is not likely to interfere with the laws of thermodynamics in the organism.

Allowing this one exception, it seems that the laws of thermodynamics can be applied to the living organism. This is not a simple matter if we consider the large numbers of different reactions which are necessary even for simple functions. Some biologists have abandoned thermodynamics and have developed arbitrary equations, probably not from disbelief in the ultimate correctness of such application, but from sheer despair of unraveling the intricately interwoven reactions.

Generally, temperature affects physical reactions, such as diffusion, conduction, and convection, not as strongly as most chemical reactions. Even with these, great differences must be recognized. The rate of reactions between ions, such as the neutralization of acid by alkali, is immeasurably rapid, and a change of this rate by a change of temperature is equally immeasurable. Photochemical reactions are almost independent of temperature: we can take snapshots in zero weather just as easily as at 99° in the shade.

But all those reactions which proceed with measurable speed show an increase in rate when the temperature is increased. This includes most reactions in organic chemistry. The final result may be the same, but it is reached much earlier at higher temperature. With most reactions, this increase is approximately the same. The rate increases about 2- or 3-fold for every 10 °C increase. We speak of this increase commonly as "temperature coefficient" and designate it with the symbol Q_{10}. This temperature coefficient applies, *e.g.*, to such reactions as the change of sucrose to invert sugar by acids or enzymes, the change of fat by alkali to soap, and numerous oxidations.

The physical chemist applies thermodynamics to this problem and uses the law of van t'Hoff-Arrhenius

$$K_{T''} = K_{T'} e^{\frac{\mu}{2} \frac{T' - T''}{T'T''}}$$

According to this, we obtain

$$Q_{10} = \frac{K_{T+10}}{K_T} = e^{\frac{\mu}{2} \frac{10}{T(T+10)}}$$

In this equation, μ is really the constant. Q_{10} will vary somewhat with temperature, because the product of the two temperatures in the exponent becomes larger with increasing temperature, and consequently the coefficient must become smaller. Table 1 shows that for an interval of 50°, this makes a difference of about 20 per cent. Such large intervals are rare in biology. Besides, the experimental error is much larger than that of the chemist because all data refer to individuals which show individuality. Therefore, the temperature coefficient is sufficiently accurate for a good deal of biological work, and is frequently used.

Table 1. Relation between the Temperature Coefficient and the Temperature Characteristic, μ.

	Temperature Coefficient Q_{10} for		
	$\mu = 12{,}286$	19,506	24,610
0–10°	2.22	3.49	4.92
10–20°	2.10	3.20	4.42
20–30°	2.00	3.00	4.00
30–40°	1.91	2.76	3.66
40–50°	1.84	2.60	3.38

Table 2 shows the application of this computation of temperature coefficients to the development and metabolism of the pupa of the mealworm. The temperature coefficients for the rate of pupal development as well as for the rate of respiration are about 2. The last column shows that the total amount of metabolism has not been affected by the temperature; only the rate has been affected.

Table 2. Pupal Development of the Mealworm, Tenebrio.

Temp. (°C)	Duration of pupal stage (hrs)	CO_2 per kg. per hour (cc)	CO_2 per kg during entire pupal stage (*l*)
32.7	139.9	427	59.3
27.25	172.5	336	58.0
23.65	234.1	252	59.1
20.9	320	186	59.6
$Q_{11.8}$	2.287	2.295	no change
Q_{10}	2.015	2.022	

Similar temperature coefficients have been found for many life functions in

Table 3. Temperature Coefficients for Different Life Functions.

Function	Q_{10}	Temp. Range (°C)
Action of liver lipase on fat	1.5–1.3	0–30
Action of malt diastase on starch	1.9–1.7	20–40
Alcoholic fermentation by yeast	2.3	20–30
Respiration of pea seedlings	2.4	10–20
Protoplasma streaming of *Valisneria*	2.3	10–20
Heart beat frequency of cat	2.1	32–38
Motion of *Paramecium*	2.4	6–16
Multiplication of *Bacterium coli*	2.75	17–29
Growth of fungus *Phytophthora terrestria*	1.9	20–30
Death of *Bacterium typhosum* by $HgCl_2$	3.0	0–40

many organisms. Table 3 gives a short selection of different types of life functions, from simple enzymic reactions to the very complex functions of motion and of growth. This would seem to indicate that a perfect analogy with chemical reactions is established, were it not for the fact that all these examples are correct only for a rather small temperature interval. As soon as this narrow range is left, irregularities begin.

These irregularities are not inconsistent. In fact, we can predict them from our general experience that all life functions cease above a definite maximal temperature and below a definite minimal temperature. Let us consider as example the multiplication of *Bacterium coli,* the rate of which has been measured by Barber (1908) under a microscope. Table 4 shows that this bacterium does not multiply

Table 4. Rate of Multiplication of Bacterium coli.

Temp. (°C)	Time required for doubling (min)	Q_{10} for each interval
5	∞	
		∞
10.0	865	
		20.5
15.6	161	
		3.74
19.5	95.6	
		4.22
25.5	40.3	
		2.10
30.5	27.5	
		1.56
35.0	22.0	
		1.57
40.5	17.2	
		0.58
45.2	20.0	
		0
50	∞	.

ove 47°. Thus, the temperature coefficient between 40° and 50° is $\frac{0}{17.5} = 0$. The bacterium is unable to multiply at +5°, and the temperature coefficient here is $\frac{161}{0} = \infty$. Thus, the temperature coefficient varies from infinity to zero in the narrow range of 45°, and it is rather obvious that a curve going from infinity to zero must somewhere equal 2 or 3. This does not sound encouraging in view of the fact that this is true of all life functions.

A less discouraging picture is obtained if we plot the temperature coefficients as a function of the temperature range. This may be seen in Fig. 1, presenting the data of Table 4 and also the measurements obtained with a large bacillus. While the curves begin at infinity and end at zero, they display a very conspicuous tendency to become horizontal, or constant, in the vicinity of 2 or 3. Knowing the usual temperature coefficients of all chemical reactions to be about 2 or 3, it seems permissible, as a working hypothesis, to assume that this nearly constant part represents the real temperature coefficient of the function. However, as the temperature increases or decreases, other processes interfere and are superposed to such an extent that ultimately the function ceases to work altogether.

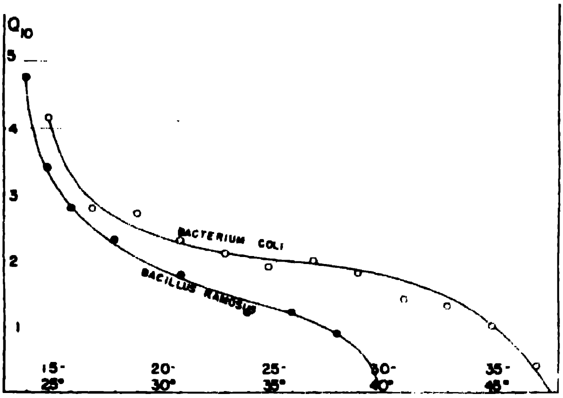

FIG. 1. Temperature coefficients of multiplication changing with temperature.

Our next task is to find the nature of the superposed processes. The reactions causing inhibition by too high temperatures are fairly well understood, at least in principle, but the factor or factors interfering at low temperatures are still a matter of widely varying speculation.

Not with all chemical reactions is the temperature coefficient near 2 or 3. There is one type of reaction with a much higher coefficient, between 10 and 100, namely the change of native proteins by heat. We observe this in the coagulation of proteins, and in the inactivation of enzymes, and of toxins. The decisive effect of such enormous temperature coefficients is well illustrated in the example of hemoglobin coagulation by heat. The data selected from extensive investigations by Chick and

Table 5. Heat Coagulation of Hemoglobin.
(*Chick and Martin*, 1910)

		Reaction constant
at 60.0°	86.5% in 90 min.	0.0215
62.6°	88.0% in 45 min.	0.045
65.6°	89.0% in 20 min.	0.105
67.7°	75.1% in 9 min.	0.164
70.4°	85.9% in 6 min.	0.350

Q_{10} = 13.8

Q_{10} approximately $\frac{90}{6} = 15$

Martin (Table 5) show the times required for coagulation of approximately the same amount of hemoglobin at different temperatures. What is accomplished at 70.4° in 6 minutes, requires 90 minutes at 60°. This means a temperature coefficient of 13.8. The same coagulation would be accomplished at 80° in $\frac{6}{13.8}$ minutes = 26 seconds, at 50° in 90 × 13.8 minutes = 20.6 hours, and at 40° in 12 days. This indicates a practically instantaneous reaction at 80°, slow reaction at 60°, and a hardly noticeable reaction at 40°. For this reason we speak of the "coagulation temperature" of a protein, and the "inactivation temperature" of an enzyme. whereas really these reactions occur over a wide range of temperatures. While such extensive extrapolations are not really permissible, we must remember that enzymes and native proteins in solution are not stable, and "deteriorate" even at room temperature.

The native proteins forming the protoplasm of the living cell coagulate by heat. In heat-killed cells, the coagulation of the protoplasm is plainly visible, especially in the dark-field. Not all of the many proteins in any one cell have the same coagulation temperature. If a vital protein whose function is necessary for cell life coagulates completely, the cell is dead. At lower temperatures, coagulation is a slow process. Let us assume that an enzyme furnishing energy to the cell, *e.g.*, an oxidase, is slowly inactivated at 35 °C. The cell can produce new oxidase, and will repair the damage. The outcome is largely a question of rates. The rate of repair rises slowly with the temperature, the rate of inactivation rises rapidly. As long as repair can keep up with inactivation, the cell will lead a normal life. In fact, in this case, all life processes will be speeded up by the higher temperature, because the same amount of oxidase will oxidize more substrate and hence furnish more energy. This will continue until a point is reached where repair can just keep up with destruction. This is the optimal temperature, the temperature of greatest life activity. Above this point, destruction is more rapid than repair, the enzyme content of the cell sinks to a lower level, and the energy furnished by the enzyme decreases. At only slightly higher temperature, destruction is so rapid that repair is negligible in comparison, and the energy supply ceases completely.

Table 6. Temperature Coefficients.

Heat Coagulation of Hemoglobin	13.8
Heat Coagulation of Egg albumin	646.0
Heat Inactivation of Pepsin	33.7
Heat Inactivation of Trypsin	17.8
Heat Inactivation of Botulo-Toxin	7.4

In this same manner, other catalysts in the cell may be destroyed, because most of the cell catalysts are similar to, or linked with native proteins. It is easily seen how, on account of the heat inactivation of the proteins and enzymes which are necessary for the various life functions, the temperature coefficient must decrease progressively when the maximal temperature is approached. At the optimum temperature, Q_{10} equals 1.

We can also see that on account of the very high temperature coefficient of this inactivation, the effect is not at all noticeable at moderate temperatures, while from the point where retardation becomes measurable to the point where the function ceases completely, it is only a difference of a few degrees. This explanation had been tested experimentally by Tammann as early as 1895, though credit is usually given to Duclaux (1899). The same principle was applied to the assimilation by plants in 1905 by Blackman, to the growth of corn seedlings by Lehenbauer (1914), to fermentation and growth of bacteria by Rahn (1915) and to respiration of animals by Potonié (1924). This explanation has been questioned by van Amstel and van Iterson (1910) who believe that the rate of enzyme reactions would show a true optimum even if the enzyme were not destroyed by heat.

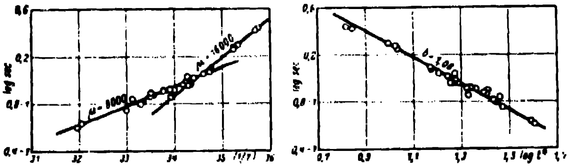

FIG. 2. Velocity of locomotion in *Paramecium* as influenced by temperature. (Glaser, 1924.) Left side: in the representation required by the formula of Arrhenius. Right side: as required by the formula of Belehradek.

At low temperatures, the deviation from the normal temperature coefficient goes in the opposite direction. As the temperature decreases, the time required for a certain process becomes progressively longer, and finally becomes infinite, *i.e.*, the process does not take place at all. For this phenomenon, no generally accepted explanation has as yet been found.

Most life functions consist of many interlinked reactions which most probably have different temperature coefficients. Since the rate of the entire function is controlled by the slowest of the coöperating reactions, it is imaginable that at different temperatures, different reactions will become the slowest. Crozier has used this principle of limiting factors to explain why we have different temperature coefficients, as may be seen from his example of the motility of Paramecium (Fig. 2).

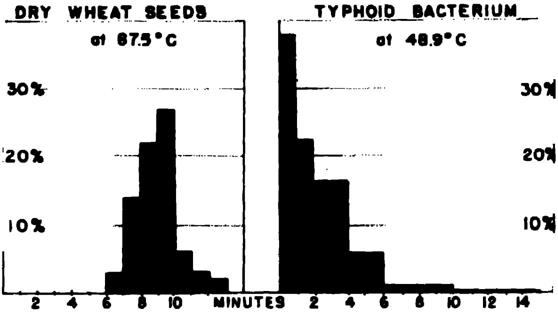

FIG. 3a. Death rate by heat in percents per minute.

Other biologists have assumed that the increasing viscosity of the protoplasm with lowering of the temperature has a retarding effect upon life processes. A third group believes that the melting points of the lipids in the cell membrane may have a decided effect upon the rate of diffusion. A striking example may be cited. The honey bee dies at +1 °C although its tissues at +1 °C still display active metabolism, because at this temperature the resorption of food from the gut is completely arrested.

A very common assumption is the accumulation of harmful metabolic products in the cells or tissues which ordinarily are eliminated or oxidized. They poison the organism at low temperature. It has been shown that plant tissues change in chemical composition after chilling.

Some biologists have given up all hope of correlating these biological phenomena with thermodynamics. They have developed empirical formulas to describe the effect of temperature which in some cases fit the experimental data better than the law of Van t'Hoff-Arrhenius. Thus, the same data on Paramecium (Fig. 2) which could be explained as belonging to two different master reactions could be fitted by Belehradek into one straight line described by a simple mathematical equation. However, we cannot regard this as an explanation because the formula is entirely empirical. It is merely a description of the experimental data in other words, and no real understanding is gained by it.

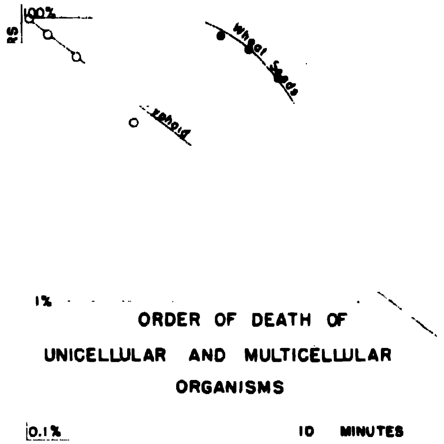

FIG. 3b.

For each of these explanations and empirical formulations, some examples can be found which fit the theory perfectly. But the examples for one theory do not usually fit the other theories. While it is natural that we continue to search for one fundamental explanation for all these effects of low temperature, it is not at all necessary that the same effects must be due to the same cause. We are quite certain that death by cold can be produced in several different ways. Thus, we may have to be satisfied that in different organisms, it may not be the same reactions which retard and ultimately stop life functions. In the same organism, different functions may be stopped by different reactions.

Besides these three so-called cardinal temperatures of life, maximum, optimum and minimum, we have two other equally important temperatures, the thermal deathpoints by heat and by cold. As a rule, thermal deathpoint means death by heat, and this temperature is fairly definite, and only a few degrees above the maximal temperature. There is no doubt that death by heat is caused by the heat inactivation of some protein, but the nature of the most sensitive protein is still debated. Some consider it to be protoplasm generally, others believe in enzymes, still others in chromosomes as the most sensitive part of the cell. A striking difference exists between unicellular and multicellular organisms in the order of death, as may be seen in Fig. 3. Large organisms can tolerate a short exposure without fatality, whereas in bacteria, the largest number dies in the first moment (Fig. 3a). As a rule, the death rate of bacteria is constant, *i.e.*, the same percentage of surviving cells dies per unit time. Consequently the logarithms of survivors plotted against time form a straight line (Fig. 3b).

While this so-called "logarithmic order of death" does not apply to multicellular organisms, it has been shown by Rahn (1936) that it may be applied to the death of individual cells of a larger organism. Fig. 4 shows the order of death of an animal or plant if death is caused by the death of 1, 2, 4 or more cells. The curve is like that of bacteria if death of the entire organism is brought about by death of one single cell; but no single cell in any plant or animal is so important. If the death of more than 10 cells is required to kill the organism, the calculated death curve agrees with the observed order of death of higher organisms.

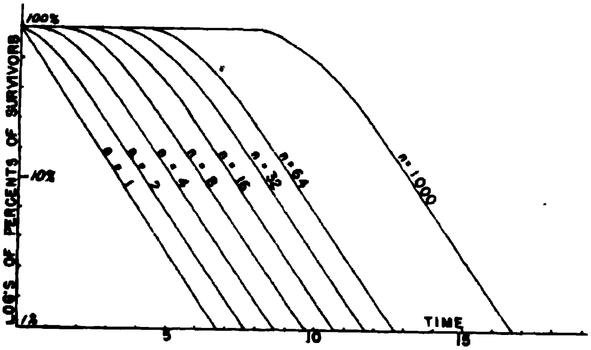

FIG. 4. Logarithms of survivors when death of the organism is caused by the death of *n* cells.

Death by too low temperatures may have a number of different causes. The tearing of the cell by the formation of the ice crystals is a simple explanation which is correct in many cases, but by no means in all. That the warm-blooded animals die when the temperature of the body drops only a few degrees below normal is well-known, and tropical plants and tropical fishes will also die if exposed for some time to low temperatures. Ice formation is not necessary for killing of these organisms. On the other hand, many trees, the needles of evergreens and the roots of perennials withstand freezing temperatures each winter, and so do the insects, worms and primitive animals, and the micro-organisms. To be sure, the test is severe, and many individuals succumb. Much depends upon the conditions of freezing. The rate is more important than the temperature as will be seen from one of the following papers, by Dr. Luyet.

An interesting observation is the shock produced by sudden heating or chilling. This affects even the simplest organisms. Plasma streaming in *Nitella* is completely stopped by sudden cooling from 20° to 3°, but not to 10°. Sherman (1934) showed that a very large percentage of young bacteria dies when suddenly cooled from 37° to 0°, whereas old bacteria are not at all affected.

The five points mentioned—minimal, optimal, maximal temperature, and the death by high and low temperature—can be observed with all animals and plants. But this by no means exhausts the effect of temperature upon life. One of the most remarkable features is the *adaptability* to different temperatures. Some individuals adapt themselves within wider limits. Still further adaptation is possible through mutation. A fairly common kind of mutation in plants is the change from diploid to polyploid types, *i.e.*, from the standard of two sets of chromosomes to more than two sets. As a rule, the polyploid types are more resistant to cold than the diploids, and this gives a special importance to the discovery that by the application of colchicin to plants, the chromosome sets can be doubled. Artificial development of hardy varieties from sensitive parents seems now possible.

Table 7. Percentage of Lethal Mutations in Drosophila compiled by Plough (1939).

	Investigators			
	Chromosome I		Chromosome II	
Temp. (°C)	Buchmann and Timofeef-Ressovsky	Birkina	Plough and Child	Birkina
− 6		0.69+0.050		2.45+0.207
+ 8			0	
144	0.087+0.0227			
18			0	
Control				
22-25	0.188+0.0464	0.22+0.032	0.82+0.194	0.83+0.108
28	0.325+0.0481		0.95+0.451	
31			2.77+1.303	
37	0.291+0.0330		1.09+0.363	

While considering artificially produced mutations, we might also consider the natural process of evolution which is brought about by chemical changes in the chromosomes of the germ cells. These changes are chemical reactions, and consequently should be expected to proceed with a higher rate at higher temperature. In other words, evolution should proceed at a more rapid pace in the tropics than in the moderate climates. While this can hardly ever be proved precisely, experiments with fruitflies have shown a higher rate of mutation at higher temperature (Table 7). A statistical survey shows a much larger number of plant species in comparable areas as the climate becomes increasingly milder (Table 8). This is also true for reptiles (Table 9) but not for the mammals whose evolution proceeds at constant body temperature in all climates. The ratio of tropical against temperate species is 9: 1 for reptiles, and only 2: 1 for mammals. Though these numbers are quite suggestive, they cannot be considered as proofs (Rahn, 1939).

Table 8. Numbers of Plant Species at Different Climates (Angiosperms only).

	Square kilometers	Latitude	Number of species
Iceland	103,000	66–70°	359
Schleswig-Holstein	23,000	54–55°	1070
Sicily	25,000	37–38°	2345

Another important feature of our general theme is the effect of the seasons upon the life cycles of plants and animals. While other factors enter here as important causative agents, *e.g.*, the intensity of light and the length of day, temperature is equally decisive, and seasonal effects can be prevented by producing an unseasonal temperature. We may think of the life cycle of insects such as grasshoppers, June beetles or Mayflies, or the blooming of flowers at a definite time of the year. These manifestations are ultimately connected and based upon the thermodynamics of chemical reactions, but so many reactions are interlinked that a detailed interpretation does not appear possible. The migration of birds is probably dominated by other seasonal factors, but the migration of certain fish

Table 9. Ratio of Species in Tropical and Moderate Climates.

Mammalia				Reptilia			
Number of species considered		Tropical	Moderate	Number of species considered		Tropical	Moderate
1	Monotremata	100	0	23	Crocodilia	100	0
50	Prosimia	98	2				
211	Primates	98	2				
44	Edentata	95	5				
438	Chiroptera	91	9	1528	Lacertilia	92	8
7	Sirenia	86	14	1384	Ophidia	88	12
111	Marsupialia	76	24				
280	Ungulata	72	28	185	Chelonia	73	27
244	Insectivora	66	34				
1284	Rodentia	59	41				
254	Carnivora	56	44				
77	Cetacea	34	66				
30	Pinnipedia	9	91				
3024	Average	69	31			90	10

may be primarily a temperature effect. Quite closely related to this is the existence of definite mating seasons in the higher and lower animals.

All previous discussion has shown that temperature affects all organisms very decidedly. It remains to be shown that organisms also affect temperature. Since the oxidation of food by high and low organisms, by animals as well as plants, liberates energy, we must expect all organisms to produce heat, though a certain share of the energy may be used for synthetic growth.

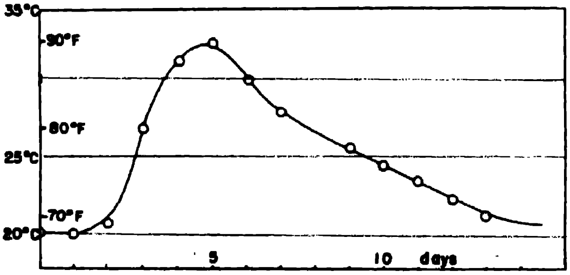

FIG. 5. Temperature of fermenting grape juice in 1500-gallon cask, at 20 °C cellar temperature.

This is easily demonstrated by preventing the escape of the heat produced. In a large cask of grape juice, the yeast produced sufficient heat by fermentation to raise the temperature of the wine 10 °C above that of the cellar (Fig. 5). Insects normally show no body temperature of their own because they give off their surplus energy by evaporation of water. In large masses, however, their body heat accumulates. The bees keep the temperature of the hive constant throughout the winter by their respiration. Plants at night have a respiration similar to that of animals, but heat does not accumulate on account of evaporation and radiation of the large leaf surfaces. However, in masses which prevent radiation, heat accumulates. Cut grass packed tightly before it is dry may develop a temperature over 50 °C; it steams and turns brown, and so do peas and sweet corn when left too long in carloads on the way to the canning factory.

The most elaborately controlled system of disposal of surplus energy is represented in the homeothermic animals. This chapter of temperature in biology, though of most vital interest to us, is not included in this general survey because the paper of H. G. Barbour deals specifically with the development of homeothermy in animals, and an entire section is devoted to heat regulation in man.

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The Vitreous State of Matter and the Devitrification Temperatures[*]

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The investigations of the last fifty years have thrown a new light on the problem of the nature of the vitreous state and on that of the relationship of this state to temperature. Since these investigations are still little known by most physicists and chemists and by teachers of physics and chemistry, we intend to state, in the first part of this paper, the fundamental principles and facts on which the modern concept of the vitreous state is based. In a second part we shall describe some of our own investigations on devitrification temperatures.

1. The Position of the Vitreous State on the Temperature Scale

Let us plot a temperature scale on a horizontal line, from the absolute zero up (*Fig.* 1). The positions occupied on this scale by the physical states of matter: gaseous, liquid, crystalline and vitreous, and the temperatures at which the passage from one state to another takes place are those indicated in the figure. Upon a lowering of temperature, a body in the gaseous state becomes liquid; it thereafter crystallizes and stays crystalline down to the absolute zero. But if, by abrupt cooling, one can bring a liquid through the zone of crystallization before it has the time to crystallize, it assumes the vitreous state and stays vitreous at lower temperatures. If a body in the vitreous state at a low temperature is warmed slowly, it devitrifies, that is, it becomes crystalline when it reaches the range of devitrification temperatures.

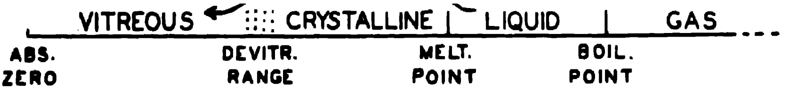

Fig. 1. Diagram representing, on a temperature scale of which the origin is the absolute zero, the four states of matter: gas, liquid, crystalline, and vitreous, and the three changes of state: boiling, melting, and devitrification. The curved arrow indicates the change of temperature for passing from the liquid to the vitreous state.

At the end of the last century (1898) Tammann[1] pointed out that the property of assuming the vitreous state is not an exceptional property of some substances, but that it seems to be universal. Out of a series of 153 carbon compounds investigated, 59, that is, 38 per cent, could be vitrified by rather simple methods.

Our investigations, which have been confined almost exclusively to aqueous solutions of organic and inorganic compounds, have shown that solutions of almost any substance which is soluble in water in the proportion of about one to four could be vitrified when immersed, in thin layers, in liquid air. Thus we obtained in the glass state solutions of sodium chloride, potassium hydroxide, calcium nitrate, sodium hyposulfite, formaldehyde, ethylene glycol, glycerol, various sugars, urea, various amino-acids, gelatin, albumin, etc.

[*] This paper has been written to bring the notion of *Vitreous-Crystalline Phase Diagrams* to the attention of *Physical Chemists*. Although it does not contain any reference to biological applications, it was classified in this chapter in view of the general field of interest of its author.

In the diagram (Fig. 1) the vitreous state appears as a "fourth state" of matter. Concerning this point the following should be noted. Some physicists (*cf.* Tammann[2]) for whom the arrangement of the molecules in the aggregate is the essential feature in the definition of the states of matter, name only two of them:

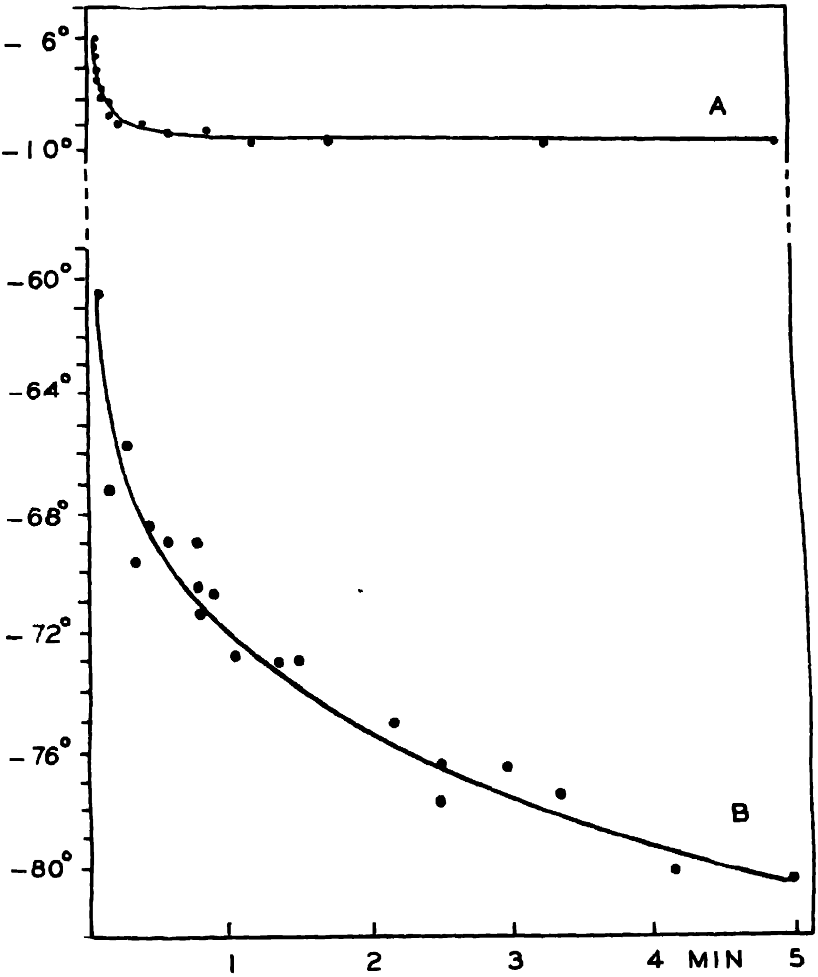

FIG. 2. Time required for complete devitrification at various temperatures; Curve A, dextrine solution, $3M/x$ (x being the unknown number of groups $C_6H_{10}O_5$ in the formula); Curve B, formaldehyde solution, 36 per cent.

the crystalline state, which possesses as a specific character an ordered arrangement of the atoms, and the amorphous state (gaseous, liquid and vitreous) in which the molecules are distributed at random in space. Most students of nature name three states: gaseous, liquid and solid, and make the vitreous state a subdivision of one of the three. Some, considering the fact that a glass possesses the hardness and cohesion of solid bodies, classify it as a form of the solid state; others, considering the deformability presented by some glasses during long periods of time, prefer to call them liquids of high viscosity; still others, considering the method of obtaining glasses and their amorphous nature, insist on calling them supercooled liquids. The definitions which have been accepted for the glass state depend, therefore, largely on the point of view taken.

It should be noticed that the concept according to which glasses are supercooled liquids does not pay due consideration to the following facts: (1) while a supercooled liquid is in so unstable a state of equilibrium that the contact with a crystal invariably produces its crystallization, a glass can be put into contact with a crystal without crystallizing. (2) A supercooled liquid has been brought *into* the zone of crystallization temperatures (Fig. 1); a glass has been brought *below* the zone of crystallization temperatures. (The change in temperature which leads to the formation of a glass is represented diagrammatically by the curved arrow in Fig. 1.) (3) A supercooled liquid does not crystallize on being warmed, whereas a glass does. It should also be noticed, however, that the first two differences vanish if one assumes that crystallization is theoretically possible at any low temperature but that its velocity, high in the region of the crystalline state (Fig. 1), decreases gradually at lower temperatures and becomes practically unobservable in the region of the vitreous state. Then the essential difference between a glass and a supercooled liquid would consist merely in the rapidity of crystallization.

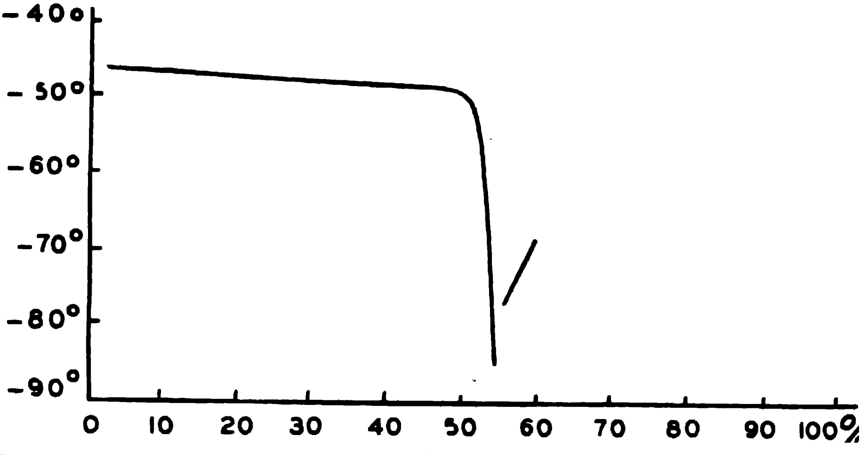

FIG. 3. Temperatures of incipient devitrification for glucose solutions of various concentrations. Abscissa: concentrations in per cent by weight; ordinates: degrees centigrade. At concentrations extending from 55 to 60 per cent a different type of crystalline structure was observed; above 60 per cent the preparations did not devitrify into crystals at any temperature.

That the velocity of crystallization decreases when the temperature is lowered, within the devitrification range (Fig. 1), is not an assumption, but a well-established fact; but that this velocity never reaches zero in the zone of the vitreous state is a theoretical view which seems to have been over-emphasized. That some glasses are unstable and devitrify after a long time has been observed; but that *all* glasses *should* eventually devitrify is by no means a safe generalization. In the study of the devitrification of aqueous solutions of carbon compounds we found that when the molecular weight of the solute is high the vitrified solution is very stable. This is illustrated in Fig. 2. The time-temperature curve of devitrification of dextrin (A) becomes rather abruptly horizontal; in other words, the vitrified solution will not devitrify in a long time at a temperature only two degrees below that at which it devitrifies completely in one minute. A vitreous formaldehyde solution is much less stable, as indicated by the slope of the curve B (Fig. 2).

A comparison of the properties of the transitions between the states of matter does not allow one to treat the vitreous state on the same basis as the three others. A gas becomes a liquid on cooling and a liquid becomes a gas on warming; a liquid crystallizes when one lowers its temperature and a crystal melts when its temperature is raised; on the contrary, while a glass crystallizes on warming, a crystal does not vitrify on cooling. In other words, boiling and melting are reversible, but devitrification is not. Furthermore, melting and boiling take place at temperatures which are practically points, whereas devitrification occurs over a larger range of temperatures. (To illustrate this difference, we indicated in Fig. 1 the boiling and melting points by the lines of separation *B* and *M*, and the range of devitrification temperatures by the zone *D*.)

2. Devitrification Temperatures

A study of the devitrification temperatures (D.T.) of sugar solutions (a description of the method employed is given below) has revealed the following facts:

(1) As the concentration of a given sugar is increased, there is, up to a certain limit, a slight gradual decrease of the D.T.: for example, the D.T. of 1*M* and 2*M* sucrose were found to be respectively −31.4° and −31.8°, the D.T. of $2M/x$ and $3M/x$ dextrin ($6x$ being the number of carbon atoms) varied from −9.4° to −9.7° (*Cf.* the curve, Fig. 3, for glucose solutions).[3]

(2) Solutions of various sugars of comparable concentrations devitrified (complete divitrification in 5 minutes) at temperatures which were progressively higher as the number of carbon atoms in the formula of the solute increased, as the following table shows:[3]

Glucose	−40.6	6 carbon atoms
Sucrose	−31.8	12 carbon atoms
Raffinose	−27.2	18 carbon atoms
Dextrin	− 9.4	6*x* carbon atoms

A study of the D.T. of solutions of carbon compounds of lower molecular weights confirmed the results previously obtained with sugars.[4] The following D.T. were observed:

Formaldehyde	−80.5	1 carbon atom
Ethylene glycol	−72.8	2 carbon atoms
Glycerol	−64.7	3 carbon atoms

(3) Solutions of gradually increasing concentrations present, besides the gradual change described above, under (1), sudden changes in the D.T. at some definite concentrations.[4] This is illustrated, for glucose solutions, in Fig. 3.

The procedure employed was as follows: A droplet of the solution was enclosed between two glass plates 0.1 mm thick, maintained at a distance of 0.1 mm from each other by two glass strips of that thickness interposed between the plates. This preparation, held in a clip, was immersed in liquid air for vitrification; it was then transported into a bath of isopentane (a liquid immiscible with water), previously cooled and maintained at a desired low temperature, in a transparent Dewar flask.

Devitrification was easily observable, the preparation becoming opaque when the material crystallized. By repeating this experiment at various temperatures and various concentrations we determined the highest temperature at which no trace of opacity could be observed in 5 minutes.

The D.T. (Fig. 3) dropped suddenly by more than 30 degrees at concentrations of 53 and 54 per cent. At concentrations from 55 to 60 per cent the D.T. were higher again (Fig. 3), but the devitrified preparations had an entirely different aspect, the crystals appearing coarser than those obtained over the range extending from 2 to 54 per cent. (The temperatures plotted in Fig. 3 are lower than those given in the table above, for glucose. In one case it was the beginning, in the other, the completion of devitrification which was observed. Glucose solutions of concentrations lower than 20 per cent could not be vitrified by immersion in liquid air; for these the "vitrification gun"[5] was used.)

The sudden drop of the devitrification temperatures of glucose solutions at 53 per cent is evidently caused by some change in the structural relationship of glucose and water at that concentration. The fact that the temperatures drop when the number of molecules of water per molecule of glucose passes from 6 to 7 suggests that it is a question of water of hydration; but the concentrations at which a similar drop in the devitrification temperatures was observed in solutions of ethylene glycol, glycerol and sucrose render this interpretation doubtful.

The curve of Fig. 3 will constitute the vitreous-crystalline phase diagram of glucose solutions when the nature of the phases which pass into the crystalline state at the temperatures indicated, above and below 55 per cent, is known.

The investigation of the phase diagrams of devitrifying solutions opens a new field which seems to be particularly promising in the study of various physicochemical problems.

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The Resistance of Living Matter to Very Low Temperatures

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The numerous studies made, since the discovery of the procedure for the liquefaction of the so-called permanent gases, on the resistance of various types of living protoplasm to very low temperatures have established the fundamental fact that some living plants and animals can be exposed to the lowest available temperatures, *i.e.,* 1° to 2° absolute, without being killed. The resistant organisms may be divided into two classes: (1) those which support desiccation and which, in the dry state, can be cooled without injury; (2) those which, even with their full water content, are not affected by low temperatures. To the first group belong spores, pollen grains, seeds, lichens, moss, some pteridophytes (Selaginella), protozoan spores and cysts, eggs like those of the brine shrimp and animals such as rotifers, tardigrades and nematodes (lower forms exclusively). The second group includes viruses, bacteria, some protozoa such as trypanosomes, some monocellular algae, yeast and fungal mycelia.[1] The cause of the resistance of dried protoplasm to low temperatures seems to be the fact that there is no water in it which can freeze. As to the cause of the resistance of organisms in the vegetative state, none is known. We assumed as a working hypothesis that, in these organisms too, the resistance to low temperature is due to the fact that the molecules of water essential to life cannot freeze out. Consequently, if it were possible to prevent the crystallization of water, low temperatures would not affect living matter. Now, crystallization can be avoided by the method of vitrification.

This method is based on the principle that a liquid crystallizes only in a limited zone of temperatures. For example, a sucrose solution crystallizes only from 0 °C to about −30 °C; at lower temperatures it becomes vitreous. Vitrification consists then in cooling the solution very rapidly so as to bring it across the zone of crystallization temperatures in less time than is necessary for the crystals to form. This can be achieved by immersing in liquid air thin layers of the material to be treated. To bring a vitrified solution back into the liquid state without letting it crystallize (devitrify) one has to warm it rapidly; crystallization can occur in the "dangerous" zone during the warming as well as during the cooling.

The water content determines the possibility or impossibility of vitrification. In general, with 50 per cent gelatin solutions we have been able to vitrify layers 0.3 mm in thickness, whereas with solutions containing 90 per cent water we could vitrify only smears a few microns thick.

Vitrification of Protoplasm[2]

We attempted to vitrify living matter by immersing it in thin layers in liquid air. To avoid devitrification we then dipped it suddenly into warm water. The material was supported by thin glass plates or mica sheets, or it was held in a film of culture medium suspended in a loop made of a thin metal wire. We tried also the method of spraying cultures into liquid air with an atomizer.

Our first series of experiments was done with *Euglenae.* The organisms were previously concentrated by centrifugation. A small drop of the concentrated culture was thereupon placed on a glass slide and left to evaporate in the air till only a swarming mass of animals remained. The preparation was then dipped into liquid air and after this into water at 20 or at 40 °C. No *Euglena* ever came back alive from the ordeal. Thinking that the organisms contained too much water, we tried to carry the evaporation still farther and to reduce the water content by adding to the droplet concentrated solutions of sugar. But concentrations which killed the *Euglenae* within one minute did not suffice to produce the desired results. The use of strips of mica instead of glass supports, to lessen the heat capacity, was likewise ineffectual. On the whole, all our attempts to revive *Euglenae* in the vegetative state were unsuccessful. Whether they were actually devitrified or frozen is uncertain.

We next repeated with *Paramecia* all the experiments made with *Euglenae*. The results were completely negative. Experiments with other ciliates, in the vegetative state, likewise gave negative results.

The same is true also of experiments with *Amoebae*. However out of 30 attempts made to vitrify *Myxamoebae* (amoebic form of the myxomycetes), 5 gave living myxamoebae whose contractile vacuoles resumed their function and maintained it for several hours.

Next we tried the *Spermatozoa* of the frog. A smear on a thin cover-glass gave negative results. A second attempt on a sheet of mica was no more successful. A third series of experiments in which the spermatozoa were previously immersed in a 20 per cent sucrose solution to be dehydrated before immersion in liquid air, yielded some motile organisms, less than 1 per cent of the number treated. By increasing the concentration of the sucrose solution to 40 or 50 per cent, we could increase the percentage of motile or non-disorganized forms to 20 per cent or more. To sum up, by employing with the spermatozoa of the frog the method of mica sheets, of dehydration in concentrated sugar solutions and of rapid warming in water at 20 °C, we obtained some living forms in each preparation. Studies on the duration of immersion in liquid air which the spermatozoa can tolerate have shown that the number of survivors and their activity are the same after five days as after three seconds. Experiments like those just described were also carried out with the spermatozoa of the rat, but not a single one could be revived.

The epidermis of the onion, a classical subject in plant cytology, seemed to be particularly appropriate for our researches, especially because of the ease with which one can obtain very thin monocellular layers. A piece of epidermis, held on a small metal fork, was immersed in liquid air and then in water at 20 °C. The vitality of the cells was tested by plasmolysis. A first series of observations furnished only dead cells. Thinking that the quantity of water present in the large vacuoles of the epidermal cells rendered vitrification impossible, we tried to reduce this quantity of water by plasmolysis in salt solutions. No cell could be revived. But we had not taken account of the fact, reported by many investigators, that a direct immersion in water after plasmolysis in a concentrated salt solution is often fatal. The invasion of the strongly plasmolysed cells by water produces a too violent expansion which causes the bursting of the protoplast. We therefore tried to warm the cells rapidly by immersing them not directly in water, but in a saline solution at 20 °C. This time we found a considerable number of cells capable of being deplasmolysed or plasmolysed to a further extent.

Moss leaves, which consist of a single layer of cells, gave results in perfect agreement with our anticipations. When devitrification was avoided the leaves always survived, whereas after vitrification and devitrification only those which had a low water content resisted immersion in liquid air. The vitality was judged by the possibility of repeated plasmolysis.

Finally we tried to vitrify muscle fibers. Bundles of five to ten fibers taken from a chloroformed frog and mounted on a metal frame, were immersed in liquid air and then in Ringer's solution at 20 °C. The fibers so treated were thereupon placed on a microscope and subjected to an electric stimulus. Some fibers, often most of the fibers present, contracted. However they ceased to respond sooner than normal fibers to repeated electric shocks. In one series of experiments vitrified fibers responded to an average of 15 successive electric stimuli, while normal fibers gave about 400 responses. The procedure followed in vitrification evidently does not kill the protoplasm but, in most of the cases, it injures it.

Discussion

The success in several revival experiments and the failure in other cases suggest that the degree of vitrification controls survival. It is probable that the vitreous state has not been actually reached in some of the organisms which had a particularly high water content. The too low temperature of the warming bath might also have been a cause of failure with some materials.

The fact that desiccated protoplasm is not injured by low temperatures is of fundamental importance to the biophysicist interested in the problem of the type of structure that matter should possess to be capable of life. The lowering of temperature alone, that is, the slowing of molecular motion, does not destroy the basic structure of protoplasm. The structural units are destroyed when water is removed from them and not when their energy is withdrawn.

Another significant fact in the study of protoplasmic structure is that desiccation brings protoplasm into a state of latent life. Living matter, which is active when some 70 or 80 per cent of its mass is water, ceases its activity but, in general, is not killed when 20 or 30 per cent of this water is removed. Further desiccation is required to destroy life. One should, therefore, distinguish two kinds of water in living matter: *metabolic water*, which is necessary for vital activity and the removal of which induces latent life, and *vital water*, the removal of which causes death.

The quantity of vital water evidently varies with the type of protoplasm. Some organisms seem unable to endure the withdrawal of more than 20 per cent of their water whereas, in some others, latent life can be maintained after all the water removable by long dehydration in vacuum desiccators has been withdrawn.

The notion that it is the removal of some water molecules which causes death results then from the study of the action of both low temperature and desiccation. It is possible that these water molecules are integral parts of the living units and that their removal is lethal by destruction of the structure. However, at present, this is a mere hypothesis.

Studies of the action of low temperature on gelatin solutions have shown that a gel which contains less than 34 per cent water cannot freeze at any temperature.[3] Comparing living units to the gelatin molecules and their escort of water molecules, one comes to the notion that those organisms in which the living units do not require a quantity of vital water exceeding a given amount (perhaps about 30 per cent) are immune to the action of cold.

In the last analysis, according to our hypothesis, cryostability or cryolability would depend on the proportion of water necessary, not for the maintenance of the metabolic activity of protoplasm, but for the integrity of the structural make-up of the living molecules.

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Minimizing Convection Currents in Electrophoresis Measurements

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In the measurement of electrophoresis by the macroscopic method, or in the Tiselius method of electrophoretic analysis, the colloidal solution is contained in a vertical U-tube. The electric current which causes the movement of the colloidal particles also causes heating of the liquid; and consequently, convection currents arise. This convection is usually the largest source of experimental error in the test and therefore limits the voltage which can be used with satisfactory results.

Tiselius[1] made an outstanding improvement in electrophoretic technic by the very simple expedient of carrying out the work at or near 4 °C. Since at this temperature water has its maximum density, the linear temperature coefficient of density vanishes, and density differences and convection currents are enormously reduced.

In the present paper the convection currents arising in the conventional U-tube electrophoresis will be analyzed theoretically. A quantitative estimate will be made of the improvement brought about by the Tiselius method. Furthermore, by precise analysis of the conditions near 4 °C, a further refinement in temperature control will be suggested which should further increase by several fold the possible speed of the test at a given level of turbulent disturbance.

Notation:

a=half thickness of flat cell or radius of cylindrical cell;
A=thermal coefficient of density, defined by Equation (1);
b=value of x or r at which the density of the liquid is a maximum;
B=second-order thermal coefficient of density, defined by Equation (2);
c=specific heat;
$F_f=1-\frac{9}{2}q+\frac{7}{2}q^3$;
$F_c=1-3q+2q^3$;
$G_f=1-6q+5q^2$;
$G_c=1-4q+3q^2$;
g=gravitational acceleration;
h=.239, conversion factor, watts to calories per second;
I=electric current density;
k=thermal conductivity;
K=electric conductivity;
P=vertical pressure gradient;
$q=x^2/a^2$ or r^2/a^2;
r=distance from axis of cylindrical cell;
t=thickness of cell wall;
T=temperature;
v=velocity of convection current;
x=distance from center of flat cell;
$\alpha=\dfrac{I^2h}{Kk_1c_p}$;

η=coefficient of viscosity;
ρ=density.

Subscripts: 1 refers to liquid;
2 refers to cell wall;
a refers to interior surface, x or $r=a$;
c refers to cylindrical cell;
e refers to exterior surface of cell;
f refers to flat cell;
m refers to maximum density of the liquid;
o refers to center, x or $r=0$;
Primes refer to the supernatant liquid.

We consider a U-tube of infinite length, which may be either rectangular or circular in cross-section. If the section is rectangular, we assume that the thickness is so small that the width may be considered as infinite. For each cell we shall analyze two cases, one in which the temperature is far removed from that of maximum density and another in which the temperature is near that of maximum density. We write the temperature density relationship in these two cases in the form of Equations (1) and (2). The general field equations governing temperature and convection currents are given in vector notation in Equations (3) and (4).

$$\rho = \rho_0[1 - A(T - T_0)] \tag{1}$$

$$\rho = \rho_m[1 - B(T - T_m)^2] \tag{2}$$

$$\nabla^2 T + \alpha = 0 \tag{3}$$

$$\eta\nabla^2 v - P - \rho g = 0 \tag{4}$$

All subsequent equations appear in pairs, the odd-numbered equations being for the flat, or rectangular, cell, and the even-numbered for the cylindrical cell. Equation (3), when written in the appropriate coödinate systems, reduces to Equations (5) and (6) respectively. In these equations we may treat the various physical properties of the solution as constants. Later, in solving the hydrodynamic equations, we must take account of the density differences, since the density differences are the cause of the convection currents. The solutions of Equations (5) and (6) are given in Equations (7) to (10).

Flat cell

$$\frac{d^2T}{dx^2} + \alpha = 0 \tag{5}$$

$$T = T_0 - \frac{\alpha}{2} x^2 \tag{7}$$

$$T = T_m + \frac{\alpha}{2}(b^2 - x^2) \tag{9}$$

Cylindrical cell

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dT}{dr}\right) + \alpha = 0 \tag{6}$$

$$T = T_0 - \frac{\alpha}{4} r^2 \tag{8}$$

$$T = T_m + \frac{\alpha}{4}(b^2 - r^2) \tag{10}$$

Equations (7) and (8) give the solution in forms convenient for dealing with temperatures far removed from that of maximum density, while Equations (9) and (10) are convenient for temperatures near maximum density. The density, expressed as functions of the temperature by Equations (1) and (2), can now be expressed, as in Equations (11) to (14), in terms of the distance from the center of the cell.

Flat cell

$$\rho = \rho_0\left(1 + \frac{\alpha A}{2} x^2\right) \tag{11}$$

$$= \rho_m\left[1 - \frac{\alpha^2 B}{4} (b^2 - x^2)^2\right] \tag{13}$$

Cylindrical cell

$$\rho = \rho_0\left(1 + \frac{\alpha A}{4} r^2\right) \tag{12}$$

$$\rho = \rho_m\left[1 - \frac{\alpha^2 B}{16} (b^2 - r^2)^2\right] \tag{14}$$

With these expressions for the variable density, we are now in a position to solve the hydrodynamic Equation (4). Written in appropriate notation, this leads to Equations (15) and (16), with the boundary conditions expressed in Equations (17) to (22).

Flat cell

$$\frac{d^2v}{dx^2} = \frac{1}{\eta} (P + \rho g) \tag{15}$$

$$v(x) = v(-x) \tag{17}$$

$$v(a) = 0 \tag{19}$$

$$\int_0^a \rho v dx = 0 \tag{21}$$

Cylindrical cell

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dv}{dr}\right) = \frac{1}{\eta} (P + \rho g) \tag{16}$$

$$v(r) = v(-r) \tag{18}$$

$$v(a) = 0 \tag{20}$$

$$\int_0^a \rho v r dr = 0 \tag{22}$$

In these equations P, the vertical pressure gradient, is not determined simply by the density of the liquid. It depends also upon the shearing stress at the wall; because the shearing stress helps support the liquid column and thereby reduces the pressure gradient below that for the static case, with no currents. P is therefore an unknown constant, and in each of the two systems of equations above, the two constants of integration and P are determined by the three boundary conditions.

In Equations (21) and (22) we may again treat ρ as a constant without losing any first order effects. We are then led to the following equations as the expressions for the velocity of the convection currents within the cell:

Flat cell

$$v = \frac{g\rho\alpha A a^4}{120\eta} G_f(q) \tag{23}$$

$$= -\frac{g\rho\alpha^2 B a^6}{420\eta}\left[F_f(q) - \frac{7b^2}{2a^2} G_f(q)\right] \tag{25}$$

Cylindrical cell

$$v = \frac{g\rho\alpha A a^4}{192\eta} G_c(q) \tag{24}$$

$$v = -\frac{g\rho\alpha^2 B a^6}{1152\eta}\left[F_c(q) - 3\frac{b^2}{a^2} G_c(q)\right] \tag{26}$$

In discussing these various solutions we may appropriately note, first, that each is the product of a constant and a polynomial in x^2/a^2 or r^2/a^2. We can obtain a rough value of the reduction in convection velocity obtained by working near the temperature of maximum density, if we simply compare these constants. As a concrete illustration of typical experimental conditions, we adopt those quoted by Longsworth and MacInnes [2] in their discussion of thermal effects in the Tiselius method. With C G S units and practical electric units, and centigrade temperatures, we then have the following set of values:

$a = .5$ cm $\quad K = .0013$
$I = .001$ amp/cm^2 $\quad \alpha = 50$
$h = .24$ $\quad A = 2 \times 10^{-4}$
$k_1 = .004$ $\quad B = 8 \times 10^{-6}$

If we now set $b=a$ and take the ratio, R_f, of the complete factor multiplying G_f in Equation (25) to the corresponding factor in Equation (23), we find, approximately, $R_f=a^2B\alpha/A=\frac{1}{8}$. Since, as will be shown later, F_f and G_f are roughly equal, this signifies that the convection currents have been reduced in general by one order of magnitude by operating at the temperature of maximum density instead of at room temperature. Treating likewise the coefficients in Equations (26) and (24), we find $R_c=a^2\alpha B/2A=\frac{1}{10}$.

We now proceed to a detailed analysis of the convection velocities indicated by Equations (25) and (26), valid in the neighborhood of maximum density. In the brackets we have the difference of two functions of q, *i.e.*, x^2/a^2 or r^2/a^2, the second of the two functions being multiplied by the factor b^2/a^2. b, the distance from the center of the cell at which the maximum density occurs, is subject to control through the adjustment of the exterior temperature. Consequently, the expressions within the two brackets can be varied, at least to some extent, and presumably can be minimized by the correct choice of exterior temperature.

Whether it would be most desirable to minimize the maximum absolute velocity, or the volume of flow in one direction, or some other property of the velocity function, is not easily decided *a priori*. Furthermore, the algebra involved in minimizing any of these functions becomes very complex. However, minimizing by exact mathematics is not necessary, for, as we shall see, by graphical analysis we can easily obtain very satisfactory minimizing conditions.

In Figs. 1 and 2 are plotted the functions F_f, F_c, G_f, and G_c. It is immediately obvious from these graphs that within the range r or $x = 0$ to a, these functions, in pairs as shown, are very closely similar. Hence, if b is chosen, as can be done, so that the brackets in Equations (25) and (26) vanish at the center of the cell, then these brackets must each have a relatively small value at all points within the cell. The actual value in each case is shown as the curve F − G in the figures.

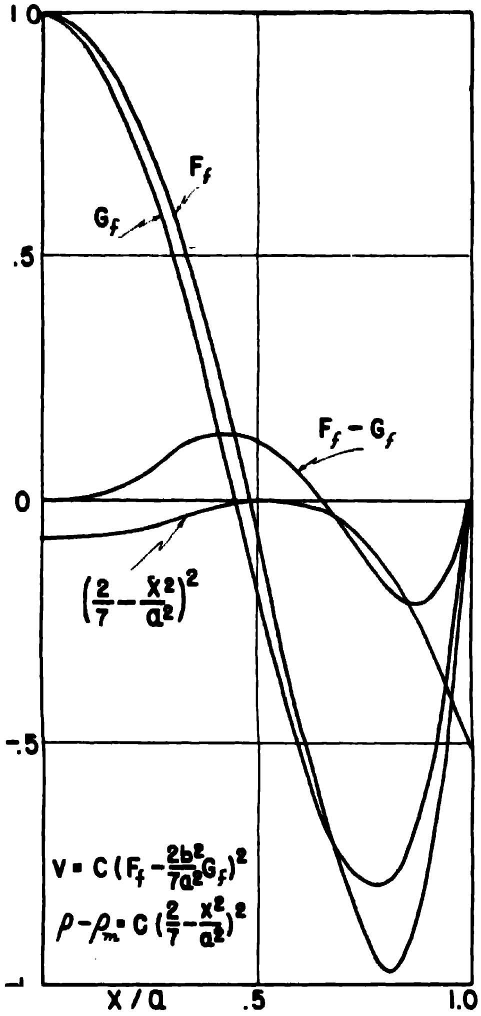

FIG. 1. Convection currents in a flat cell.

The current consists of two components, F_f and G_f, the latter occurring, in Equation (25), with a negative sign and a factor $7b^2/2a^2$. The point of maximum density, b, is subject to control and can be adjusted so that the factor multiplying G_f has the value -1. The resultant current is then $F_f - G_f$, shown in the figure. The departure from maximum density in this case is proportional to $(2/7 - x^2/a^2)^2$.

In Fig. 1 the maximum value on the curve $F_f - G_f$ is about $\frac{1}{8}$ of the maximum value on either of the original curves. Similarly, in Fig. 2, the maximum value on the composite curve is about $\frac{1}{10}$ of the maximum value on either of the two original curves. We therefore see that by precise and correct adjustment of the point b, it should be possible to reduce the convection current velocity by another order of magnitude as compared to the velocity when the temperature at the surface or at the center of the cell, for example, is the temperature of maximum density.

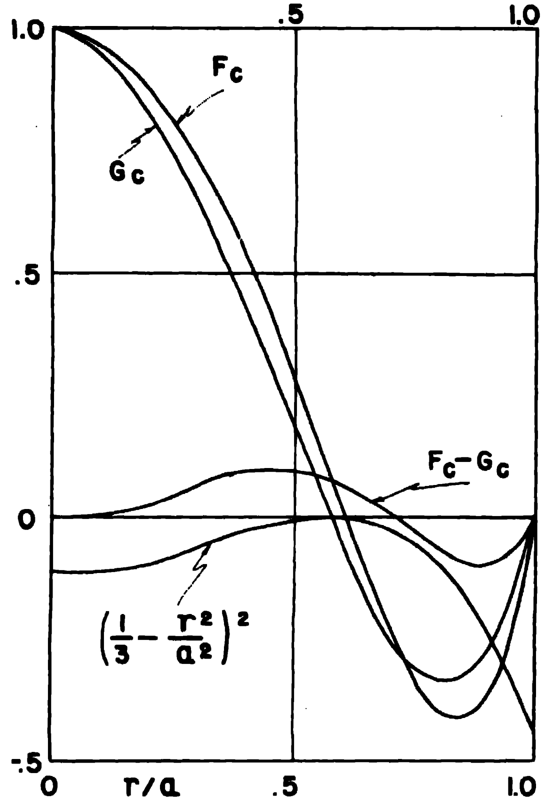

FIG. 2. Convection currents in a cylindrical cell.

The current consists of two components, F_c and G_c, the latter occurring, in Equation (26), with a negative sign and a factor $b^2/3a^2$. The point of maximum density, b, is subject to control and can be adjusted so that the factor preceding G_c has the value -1. The resultant current is then F_c-G_c, shown in the figure. The departure from maximum density in this case is proportional to $(1/3-r^2/a^2)^2$.

In order to determine what must be the temperature exterior to the cell in order to obtain these optimum conditions with respect to convection, we return to Equations (9) and (10) and insert the appropriate values for b^2, which are: $b^2=2a^2/7$ in Equation (9) and $b^2=a^2/3$ in Equation (10). Also, setting x or $r=a$, we obtain, for the temperature at the interior surface of the cell, Equations (27) and (28).

Flat cell

$$T_a \quad T_m - \frac{5\alpha a^2}{14} \tag{27}$$

Cylindrical cell

$$T_a = T_m - \frac{\alpha a^2}{6} \tag{28}$$

The further drop in temperature through the glass walls of the cell is determined by an easy application of Equations (5) and (6), with $\alpha=0$. We thus find expressions for the exterior temperatures as given in Equations (29) and (30).

$$T_e = T_s - \frac{I^2hat}{Kk_2} \tag{29}$$

$$T_e = T_s - \frac{I^2ha^2}{2Kk_2} \ln \left(1 + \frac{t}{a}\right) \tag{30}$$

By combining these two equations with the two previous equations, repectively, we obtain expressions for the exterior temperature in terms of the temperature of maximum density and other constants of the system.

Flat cell

$$T_e = T_m - \frac{I^2ha}{K}\left(\frac{5a}{14k_1c\rho} + \frac{t}{k_2}\right) \tag{31}$$

Cylindrical cell

$$T_e = T_m - \frac{I^2ha^2}{K}\left[\frac{1}{6k_1c\rho} + \frac{1}{2k_2}\ln\left(1 + \frac{t}{a}\right)\right] \tag{32}$$

These two equations then determine for the experimentalist that exterior temperature at which convection currents are reduced to a minimum, this temperature being expressed entirely in measurable quantities. In this connection it may be pointed out that the thermal conductivity of the glass, k_2, can be obtained readily by measuring the difference in the temperature inside and outside the cell while a constant electric current is flowing through the cell and the water in the cell is continuously stirred to keep it at uniform temperature.

It is customary in using the U-tube electrophoresis cell to have, as a supernatant liquid above the colloidal solution, a liquid which differs slightly from the colloidal solution in density and in other physical properties. The movement of the boundary between these two liquids is the quantity to be measured in the test. Hence the distortion of this boundary by convection currents is particularly to be avoided so far as possible. We must therefore consider what effects will be produced by the slight differences in properties that occur in crossing this boundary. If we write Equations (31) and (32) with primes to indicate the constants for the supernatant liquid, and then combine each of these two resulting equations with the corresponding original Equations (31) and (32), respectively, we obtain the two Equations (33) and (34).

Flat cell

$$T_m - T_m' = I^2ha\left[\frac{5a}{14}\left(\frac{1}{Kk_1c\rho} - \frac{1}{K'k_1'c'\rho'}\right) + \frac{t}{k_2}\left(\frac{1}{K} - \frac{1}{K'}\right)\right] \tag{33}$$

Cylindrical cell

$$T_m - T_m' = I^2ha^2\left[\frac{1}{6}\left(\frac{1}{Kk_1c\rho} - \frac{1}{K'k_1'c'\rho'}\right) + \frac{1}{2k_2}\left(\frac{1}{K} - \frac{1}{K'}\right)\ln\left(1 + \frac{t}{a}\right)\right] \tag{34}$$

In these equations the factors in the right members not included in the parentheses have the same value above and below the boundary. If the other constants in these equations are chosen or adjusted so that the equations are satisfied, we then know that both above and below the boundary the point of maximum density in the liquid occurs at the same value of b; *i.e.*, $b = a\sqrt{\frac{2}{7}}$ or $\frac{a}{\sqrt{3}}$, respectively. The constant which changes most in crossing the boundary is usually the electrical conductivity, K. As a first experimental approximation, then, it may be sufficient to correct this situation and adjust $K'=K$. If on the other hand the temperature of maximum density of the supernatant liquid differs much from that of the colloidal solution, other and more complex adjustments will have to be made. In any case, a small difference in density, sufficient to help keep the boundary surface level, can probably be tolerated.

In conclusion it may be said that while the adjustment indicated by Equations (31) to (34) may appear somewhat complex, it is likely that they can be accomplished without great difficulty; and, if proper regard is paid to these conditions, we may anticipate that the speed or precision of the Tiselius cataphoresis method may be improved several fold beyond that already accomplished so neatly by Tiselius himself. It should be noted, however, that, if the convection velocities are reduced by a factor of 10 by a temperature adjustment, it does not follow that the voltage or current density can then be increased ten-fold without exceeding the original degree of turbulence. If we take as a measure of turbulent disturbance the ratio of turbulence velocity to electrophoretic velocity, c, we deduce from Equations (25) or (26) that v/c varies as I^3. Therefore the factor by which voltage or current density could be increased in the case considered would be $\sqrt[3]{10}$, or 2.15. This will be true regardless of whether the temperature adjustment is from room temperature to near the temperature of maximum density, or from the latter approximate adjustment to the exact temperature required by Equations (31) and (32).

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The Development of Homeothermy in Animals

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Homeothermy in animals is the maintenance of an even temperature in the optimum range for biological activity. No factor has contributed more to the superiority of the highest forms of life. The body maintains a proper balance between heating and cooling by control of both processes. As in the case of most engines, energy including heat is derived from organic fuel, and cooling is achieved by a substance ranking very high in two physical properties: specific heat and heat of evaporation. This substance is water.

Available moisture tends, in a relatively dry environment, toward stabilization of temperature even in the inorganic world. A familiar example is the relatively even temperature of the sea as compared with the land. In a dry environment any moist object, for example damp soil, when exposed to a rising external temperature, gains in heat-dissipating capacity by virtue of increasing vapor pressure. Thus increasingly more heat is lost by evaporation and the soil gains heat much more slowly than the air. Conversely it cools off less rapidly when the outside temperature falls.

In this way, as well as by its relatively large storage capacity for heat, water confers upon all things a certain degree of thermal stability. Ova of true homeotherms, if unprotected, would be scarcely better off than say a moist log. But animal life is associated with oxidations, and the heat thus continuously produced maintains a body temperature above that of the environment, which yet remains the determining factor.

The tropical seas, whence life seems to have arisen, afford a temperature range which is optimum because it approaches the maximum temperature limit free from irreversible changes such as protein coagulation. Emerging from the evenly warm ocean to the more capricious climates of the air, heat derived from food and activity became essential to the up-keep of bodily temperature.

As one follows the development of the race (phylogeny) a parallelism is found in the evolution of each individual (ontogeny). The mammalian embryo may be said to offer in "pocket edition" the history of the race. The developing ovum. although moist, and productive of heat, exhibits no true homeothermy, but within the womb enjoys a "private pond" of constant tropical temperature. Here it flourishes until, as happened to its first amphibious ancestor, the time comes for emergence to the dry land.

The developing poikilotherm, as well as the homeotherm, exhibits an increasing heat production per mass of tissue as surface area relatively decreases. At some time, either before or after hatching or birth, but definite for each species, the peak is reached; thereafter, metabolic rate tends to parallel surface area.

Homeothermy differs in degree in various species and develops gradually in the individual. It is essentially lacking in reptiles as well as amphibians although well developed in birds. Among some lower mammals there is such poor resistance to cold that the body temperature lies scarcely more than half way between that of the poikilotherm and the true homeotherm. This was shown for the Australian ant-eater by C. J. Martin. Heat production in response to cold (possibly faintly discernible in amphibians) becomes an effective weapon as the basal regions of the brain become functional in the race or individual. The same applies to mechanisms which provide for heat loss. Elimination of the function of the hypothalamus, either by its actual removal from the brain base or by anesthetics such as ether or alcohol, changes a homeotherm into a poikilotherm, at least temporarily.

Heat production is provided for in animals by oxidation in muscles and internal organs (of the latter, the liver is the largest and most effective). Heat loss is accomplished by evaporation of moisture and by mechanisms favoring radiation of heat. Evaporation of moisture is provided for by all surfaces exposed to air, namely, the lungs and respiratory passages and the skin. Evaporation from the respiratory surfaces is speeded by panting (polypnea), a mechanism first seen in marsupials (Pearse and Hall),[1] and the skin provides moisture continually by "transpiration," and in hot environments by sweating. Radiation and convection are favored by increased blood flow through the skin. This is accomplished through tremendous variations in the caliber of the blood vessels. No mechanical engine exhibits either this feature or any other automatic device for withdrawing its radiator to its interior in response to a cold environment!

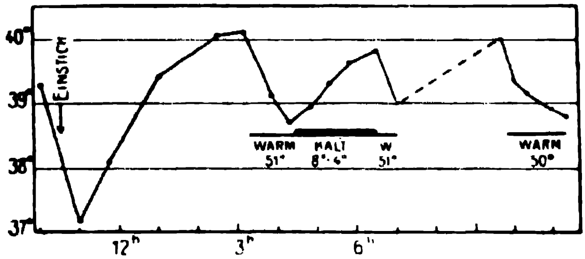

FIG. 1. Effect on body temperature ot a rabbit of warming and cooling the base of the brain in such a way as to influence the intact hypothalamus. Ordinates, degrees centigrade; abscissae, time. Arrow indicates the moment of aseptic introduction of apparatus, the fall in temperature at this time being due to an anesthetic.

Dubois [2] has compared the retirement, in cold conditions, of much of the circulation to more internal regions to "putting on a suit of clothes," and states that Hamilton and Barbour have found under similar conditions a migration of water from the blood into the tissues, thus padding the "suit of clothes."

There is also a pilomotor, or hair-moving mechanism which, in many species, tends to diminish radiation by roughing of the fur or feathers. This increases insulation by the provision of an extensive system of air spaces. Next to the voluntary measures mentioned below, the acquisition of a furry coat seems to be the most important protection against cold.

Homeotherms possess a thermostat-like mechanism in the base of the brain. Temperature changes applied to the skin are reflected here through the medium of nerve impulses. This central mechanism is also influenced by the temperature of the blood which passes through it. Cold evokes the heat production processes while heat arouses the heat loss mechanism. Both cold and heat also accomplish some supression of the mechanism which produces the undesired group of results.

The influence of cold and heat applied directly to the base of the brain was demonstrated by my work in Professor Hans Meyer's laboratory in 1912.[3] Hot or cold water was allowed to flow through a tube in the brain of a rabbit in such a way as to influence the untouched region of the hypothalamus. Cooling this region increased the rectal temperature, the reason for which could be seen in the increased tenseness of the muscles, with shivering and the paling of the rabbit's ears as the blood was withdrawn from these radiating surfaces. Warming, on the other hand, produced a fall in rectal temperature accounted for by the flushing of the ears with a lively blood flow and the presence of marked panting (Fig. 1). In mammals the intimately related anterior and posterior portions of the hypothalamus have become concerned with protection against heat and cold respectively. The division of the hypothalamus of the monkey into these two portions is indicated in Fig. 2, which represents an internal view of one-half of the monkey brain. The functional separation of these two parts was suggested by Hans H. Meyer's[4] dual center theory. In 1913, he first postulated anatomical separation of so-called "heating" centers and "cooling" centers. Bazett and his collaborators[5] showed that the so-called heating center corresponded to the posterior hypothalamus while suggesting the anterior hypothalamus as the locus of the heat-loss mechanism. Ranson and his collaborators[6] have provided ample confirmation of the latter conception by beautifully controlled heating experiments upon cats, as well as by destruction of small areas in cats and monkeys.

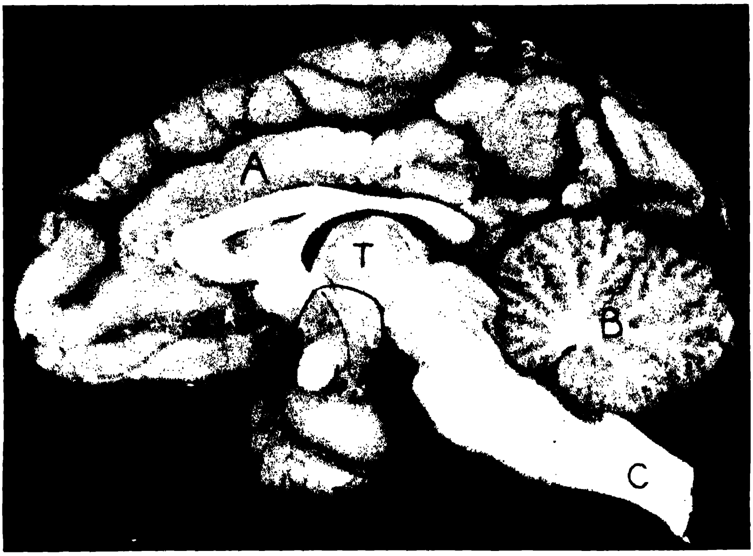

Fig. 2. Hemi-section of monkey brain. A, cerebrum; B, cerebellum; C, spinal cord; T, thalamus. The continuous line indicates the boundaries of the hypothalamus, which is divided into anterior (left) and posterior (right) portions by means of the broken line (courtesy of H. S. Burr).

In our laboratory[7] the distinction has been clearly brought out in experiments devised to locate water shifting reflexes in the cat or monkey brain. Fig. 3 illustrates the hypothalmic lesions of the same monkey shown in Fig. 2. In this enlarged sketch have been placed lines indicating the direction of certain transverse sections. After operations upon outlying points, the temperature of the monkeys in a room at about 25 °C was found normal on the following day. The four underlined figures represent abnormally high temperatures, 39.4 and 39.6 °C, which were exhibited for a number of days by monkeys with lesions in the anterior hypothalamus. Large figures indicate abnormally low temperatures which were exhibited by animals with lesions in the posterior hypothalamus and in paths descending therefrom. Good heat regulation was therefore shown by animals with injuries in outlying regions; poor regulation against cold in animals with lesions in the heating center and its paths; and poor regulation against heat in animals with lesions in the cooling center. The lowest-placed figures in the chart illustrate the result of removal of the pituitary gland in three animals. It will be seen that two of these had some difficulty in protecting themselves against cooling.

In the same series of experiments water-shifting control was found in the anterior hypothalamus.

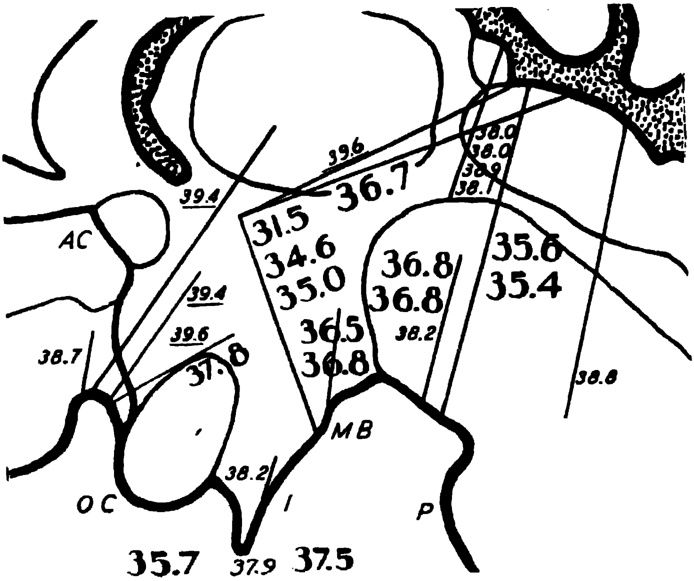

FIG. 3. Schematic enlargement of hypothalamic region of monkey brain shown in Fig. 2. Straight lines indicate transections of the brain at the levels indicated. Figures illustrate the resulting temperatures of the animal during the next one or two days. Small figures represent normal temperatures; underlined figures, abnormally high temperatures; large figures, abnormally low temperatures. Interference with heat-loss mechanisms is indicated in the anterior hypothalamus, and with heat saving mechanisms in the posterior hypothalamus. The three figures at the bottom indicate the results of removal of the pituitary gland.

Voluntary activity of various sorts affords additional protection against heat or cold and in the broader sense, may be included as a manifestation of homeothermy. Thus, heat may be produced voluntarily by increased muscular activity and huddling, while heat loss may be diminished by the introduction of insulation, as with clothing and shelter.

Heat loss mechanisms become effective later than those for heat production. At birth or hatching neither are present in some species (mouse or pigeon); others (rabbit, man, cat) exhibit only heat production responses. Control of both heat production and loss at birth or hatching may also occur (guinea pig and chick). Thus the so-called "higher" species do not necessarily show the better development of heat regulation capacity. Man, for instance, occupies an intermediate position among mammals between the well-developed guinea pig and the helpless mouse at the time of birth. Insulation mechanisms offer further examples of this. For instance, so-called nidicolous birds are distinguished from nidifugous birds by the necessity of providing nests after hatching. Pigeons, pelicans, etc., (Fig. 4) are born naked and helpless, depending upon nests for heat regulation, whereas the new-born chick emerges with a fine downy coat and a capacity to resist elevated as well as depressed environmental temperatures (Fig. 5). The apparently superior chick, however, belongs to a race which does not possess the intelligence to provide for young, exhibited by nidicolous species. Similarly, the human baby, half poikilothermus as he is, can claim superiority for his kind above the new-born well-furred guinea pig, for the human species has the intelligence to provide an environment of suitable temperature for a long period after birth.

FIG. 4. Young brown pelicans in scant plumage, poorly equipped for heat regulation long after hatching (C. W. Beebe).

FIG. 5.

Chick of jungle fowl one day old, hatched covered with down (C. W. Beebe).

Well-developed heat-loss mechanisms, as mentioned above, tend to circulate the heat-bearing blood through the body surface. The blood-flow increase may even be fifty-fold in the human limb. Experiments will now be cited showing how

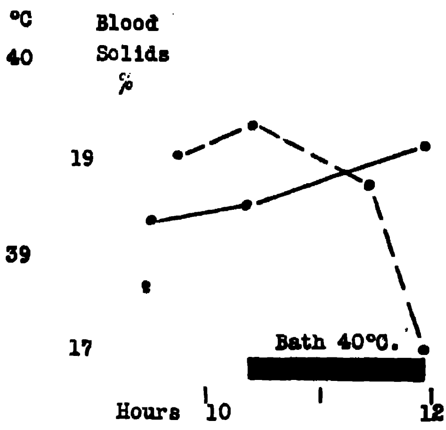

Fig. 6.

Effects of hot-bath upon blood solids percentage of a dog. Ordinates, body temperature (continuous line) and blood solids percentage (broken line) ; abscissae, hours.

important a role is played by water in connection with this mechanism. The effect of a warm environment is to cause reserve water to be mobilized from the various tissues of the body into the blood-stream, thus increasing the volume and motivating the transport of heat. An effect of this sort in the blood is shown in Fig. 6, illustrating an exposure of a normal dog to a bath at 40 °C for an hour and a half. As shown by the broken line, the blood solids decrease by more than ten per cent during this period, indicating a corresponding addition of water to the blood.

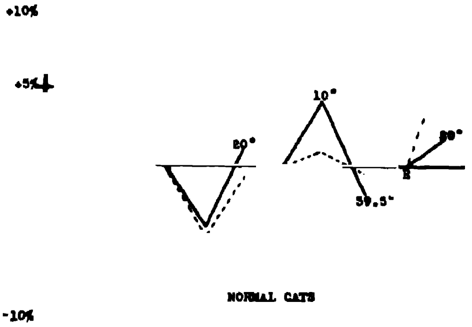

Fig. 7. Percentage changes in osmotic pressure and specific gravity of plasma of normal cats exposed to cold and warm baths. Continuous lines, osmotic pressure; broken lines, specific gravity. Ordinates, time (each exposure lasted about 15 minutes, its termination being indicated at point where temperature readings are given) (Barbour and Gilman).

The blood dilution response to heat is, however, not determined by temperature alone, but rather by the "cooling power of the environment" which is compounded by four factors: temperature, humidity, air-motion and external radiation conditions. Lozinsky[8] studied blood-concentration in dogs in which the last two factors were kept constant. He found blood dilution most marked at 28 °C in moist atmospheres, but at 38 °C in dry atmospheres. Hemingway and Barbour[9] investigated by diathermy the amounts of heat necessary to affect the blood concentration of dogs. In three-hour experiments they found, using the basal metabolic rate as the unit, that application of heat at the rate of 1.0 B. M. R. produced only a substantial dilution of the blood, 2.0 B. M. R. dilution followed by concentration and 3.0 B. M. R. concentration only.

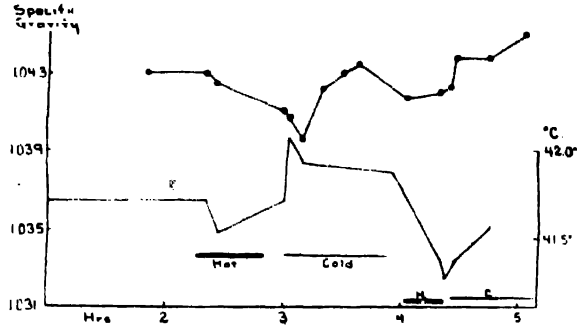

FIG. 8. Effects of heating and cooling the brain of a rabbit on body temperature (light line) and whole blood specific gravity (heavy line). Ordinates, specific gravity and temperature; abscissae, hours. Heavy straight line, brain heated; light straight line, brain cooled (Barbour and Aydelotte).

The water content of the blood is also reflected in the specific gravity and osmotic pressure of the serum. Dilution of the blood by warm baths and concentration by cold baths in cats is illustrated in Fig. 7, in which the percentage changes in osmotic pressure and specific gravity are expressed as ordinates. The temperature of the bath is shown just after the effect which it produced in about fifteen minutes (Barbour and Gilman).[10] It is thus evident that blood-water

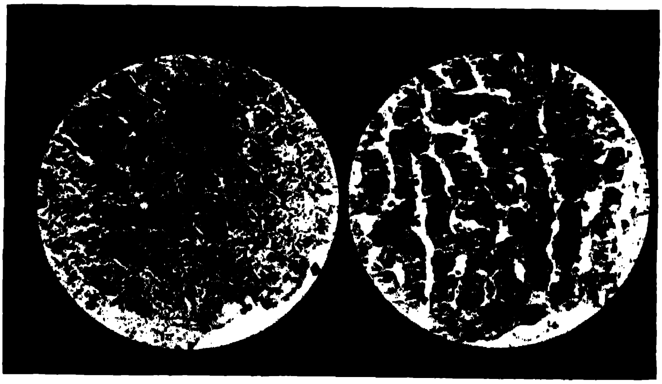

FIG. 9. Liver cells during cooling and heating of the brain, respectively. Left-hand section shows swollen cells during brain cooling (Barbour and Aydelotte).

homeostasis (maintenance of a constant level: Cannon) becomes sacrificed in the service of temperature homeostasis.

The blood concentration changes are also brought about when heat is applied centrally, as in the rabbit so treated by Barbour and Aydelotte[11] (Fig. 8). When heat was applied to the brain the rectal temperature fell, as did the specific gravity of the blood, whereas cold caused a rise in temperature, together with increased blood concentration as indicated by the specific gravity. The same investigators endeavored to trace the source of extra water received in the blood on heating and its fate on cooling the organism. The organ in which changes were best demonstrated was the liver, which exhibited decreased solids percentages after cooling, but increased solids after heating the brain. Such effects were shown histologically, as the swelling of the cells with cold (Fig. 9, left) and the shrinkage of the cells when the heating procedure was applied (Fig. 9, right).

Water, by virtue of its heat capacity, is thus used for heat storage and transport; it is also of some value in the insulation of the surface against cold during withdrawal of the circulation to deeper regions. Mechanisms have been developed for pouring it over body surfaces, for evaporation. In environments above 31 °C the degree of heat-loss in man becomes proportional to the area of "wetted surface" (Gagge, Herrington and Winslow).[12] Sweat secretion is the chief mechanism concerned but, in panting, saliva (*e.g.*, on the dog's tongue) becomes important. The respiratory mechanisms, when aroused to panting by a hot environment, further the external disposition of water vapor arising from the lung surfaces.

During conservation of heat in moderately cold environments we have found the blood plasma concentrated equally with respect to proteins and electrolytes. This indicates the shifting of water alone. Here metabolic stimulation seems to play a role by the osmotic effect of its end products in the body cells and thus becomes a source of heat saving as well as heat production. Evidence of coödination between metabolic stimulation and water shifting is seen in the parallelism between the curves relating these respective responses to environmental temperatures (Barbour and Gilman).

The metabolic stimulation as well as the circulatory redistribution depends in part on the adrenal glands. Cannon's work[13] points to the sympathetic nervous system, in which the adrenal glands play such an outstanding part, as the first line of defense in the production of heat for protection against a cold environment. According to Cannon the second defense is shivering. This was indicated by administration of ice or ice-water to cats in such a way as to produce internally a "heat deficit" of 900 calories. Normal cats thus treated showed little or no shivering, but cats which had been deprived of the adrenal glands and the other mechanisms of the sympathetic system showed pronounced shivering under circumstances otherwise comparable. In the phylogenetic scale the adrenal glands first show complete development in the lower homeotherms (birds). In poikilothermous animals the adrenals are but rudimentary.

A pre-shivering phenomenon has been discovered by Bronk[10] in the progression of groups of nerve impulses detectable electrically but not consummated by muscle movements. As they gradually increase in intensity shivering begins. There is no evidence that they are related to the heat-producing activity of the adrenal hormone.

The fact that the metabolism may fail to rise until 5 to 10 minutes before the onset of chills is believed by Hardy, Milhorat and DuBois[14] to cast doubt upon regulation against cold before the active muscular mechanism comes into play.

Other endocrine glands have also become of importance to heat regulation. Animals in which the thyroid is well developed are best able to acclimatize themselves more or less permanently to cold environments. Rats exposed to cold for a few days exhibit proliferation of the thyroid gland. The cells become increased in size and altered in shape. Apparently this makes it possible for the glands to adjust the basal heat production of the body to a higher level. Uotila[15] has recently shown that for the thyroid to perform this function requires the production of the so-called thyrotropic hormone which is manufactured by the anterior portion of the pituitary gland. It is of extraordinary interest that this gland receives innervation from the hypothalamus, which in turn receives, as mentioned above, the impulses resulting from external cold.

In closing, let us return to water evaporation as a primitive method of heat regulation requiring no accessory mechanism. The automatic partial regulation of the moist log finds its counterpart in the world of the poikilotherms. F. G. Benedict's [16] studies of the python show that in this creature's fasting periods (which, according to C. J. Martin, sometimes last over three years without elimination of muscular power) its temperature often falls below that of the environment by several degrees. This is because the python partakes essentially of the nature of a wet-bulb thermometer. Soderstrom and DuBois [17] found that normal men and patients with various diseases exposed to an average temperature of 22 to 25 °C lose on the average 24 per cent of their calories through vaporization of water, the loss per day averaging seven hundred grams for an adult. They state that "under a large variety of conditions the human body responded to the laws of physics and resembled so much meat." Carrying further this line of reasoning, it is of interest to estimate quantitatively the role of diminished evaporation in the cold as a measure of protection against cold. Data provided by Rubner [18] many years ago allow us to make such a calculation in several ranges of temperature. Using his results on dogs at 25 °C as compared with dogs at 15 °C, Fig. 10 has been derived. The upper bar represents the total heat production, likewise the total heat loss, of the animal at 25 °C. This may be called 100 per cent of the calories, of which 24.4 per cent when eliminated were carried off by water evaporation. Now, on reduction to 15 °C the animal protected itself by increasing heat production to 116.2 per cent of the original caloric value. At the same time it will be noted that only 16.1 per cent of the original caloric value was eliminated by water evaporation. This figure includes a correction for the environmental humidity change.

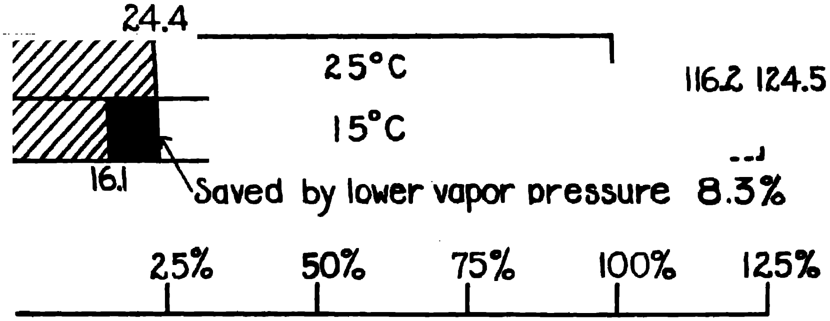

FIG. 10. Upper bar: caloric production and loss (both 100 per cent) in dogs at 25 °C. The 24.4 per cent cross-hatched area on the left indicates the proportion of caloric loss by water evaporation from the body surface. Lower bar: caloric production and loss (both 116.2 per cent) at 15 °C, environmental. Heat loss by evaporation 16.1 per cent of original caloric loss at 25 °C. Black area: saving of loss by evaporation due to lowering vapor pressure, accounting for a temperature fall of 7 °C at the evaporating surfaces. Broken line: area of excess heat production which would have been needed without the saving due to lower vapor pressure. (Calculated from data given by Rubner.)

It may now be assumed that the reduction in evaporation, saving 8.3 per cent of the total heat loss, was due to cooling. In the first place, the temperature loss which would, by lessened vapor pressure, provide such a restriction in evaporation, will be found to constitute only two-thirds of the environmental temperature fall indicated. As the temperature at the average point of evaporation on the body surface is necessarily considerably warmer than that of the environment, and as the internal body temperature remains constant throughout, this hypothetical average surface-temperature may well fall one-third less than the environment in the temperature range concerned.

Factors other than direct cooling which suggest themselves in accounting for reduced evaporation may therefore probably be considered unimportant. For example, the hair-raising response which roughens the fur has been suggested as an impediment to evaporation. Curling up of the body in the colder environment also might reduce evaporation. However, in the author's experiments in which cats were changed from a 23 °C environment to one of less than 0 °C with a seven per cent reduction in water loss, the animals at both temperatures lay perforce in unchanged position, curled up in a large bell jar. Rubner found *less* water loss reduction in dogs at from 0 to 15 °C than at higher temperatures, owing to increased respiration associated with the high metabolic rate induced by the cold. Such respiratory increase was observed neither in our cats nor in Rubner's dogs in the experiments detailed above. Still another factor, increased environmental humidity, has been eliminated in the foregoing example by Rubner, who corrected the water-loss reduction for the known change in relative humidity.

Finally, the author's finding in such experiments of an osmotic pressure increase in the blood of the order of five per cent suffices to account for a total vapor-pressure reduction of only a fraction of a millimeter. The five per cent blood volume decrease thereby indicated is, however, of major importance in limiting radiation as explained above.

Other features of heat regulation are perhaps deserving of some of the attention devoted here to the behavior of water. It is, however, well to note that, in spite of the development of elaborate mechanisms for homeothermy, the thermal stability imparted by water is still important. Rubner's dogs exposed to 15 °C would obviously have had to produce a 24.5 per cent increment of heat instead of a 16-per cent increment, were it not for the old method of heat regulation of the inanimate world, namely, decrease of the vapor pressure of a cooled moist surface.

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Heat Production and Thermal Conductance in Small Laboratory Animals at Various Temperatures

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The nude human being can tolerate an environmental temperature decrease of 4 to 5° below 29 °C without any conspicuous change in heat production or internal body temperature.[5] It is reasonably clear that this is possible in part through vasomotor control of the thermal conductance of the peripheral tissues,[2,5] and in part through restriction of the physical adjustments in tissue temperature gradients to peripheral and relatively non-vital parts of the organisms. The addition of clothing greatly extends this range of approximate thermal neutrality.

Smaller warm-blooded species such as the guinea pig, rat, and mouse are much more vulnerable to the effects of temperature changes in the environment, and it has been known for years that these species show large increases in heat production at temperatures below 28 to 30 °C,[4] a fact which has been sensibly related to species differences in surface per unit of mass. Much of the scientific discussion of this point is an intimate part of the perennial problem of an adequate standard of heat production for comparative physiology, and is relatively ancient history. In a brief report it is not possible to discuss the moderate revitalization of this argument which seems likely to grow out of recent concentration on the biophysical aspects of heat loss, as contrasted with earlier emphasis on studies of heat production.

It will be sufficient to say that in the present study the aim has been to relate the heat production of the guinea pig, rat, and mouse, as expressed in terms of a consistent estimate of surface area, to standard operative temperatures[2] in the range from 13 to 35 °C with correlated observations on mean surface temperature, rectal temperature, internal thermal conductance, and the constant of external heat loss. In a preliminary manner the study parallels some of the recent work by Bazett, Burton, DuBois, Gagge, Hardy, Herrington, Winslow, and others on human heat loss.

Our observations of heat production represent approximately 70 six-hour periods on mature males of each species, as obtained after adaptation and fasting periods, at the experimental temperature, of 12, 18, and 24 hours for mice, rats, and guinea pigs, respectively. At all other times the animals were caged at 24 °C. All experiments were conducted between 10:00 A.M. and 4:00 P.M.

Metabolism was measured by the Haldane gravimetric method in a group metabolism chamber which accommodated 50 mice, 10 rats or 6 guinea pigs. The chamber was contained in a controlled temperature room which could be regulated within ±.25 °C. Chamber walls of thin copper and individual caging in small wire-screen hemispheres insured equivalence of air and radiation temperature, and air movements within the range from 12 to 20 feet per minute, conditions which satisfied our laboratory criterion of standard operative temperature. No correlation of R. Q. with test temperature was found, and all data were computed on the basis of the mean R. Q. for a given species. Mean R. Q.'s for the three species varied from .74 to .76. Activity during the experimental period was restricted only by the small size of the individual cages, a feature which should reduce random exploratory behavior without interfering with activity which may be an integral part of the response of these small animals to environmental temperature. In standardizing heat production in terms of estimated surface area, the formula $9.0 \times W^{2/3}$ has been used for guinea pigs and rats, and $9.1 \times W^{2/3}$ for mice (Benedict, 1938).[1] Other choices could be logically defended, but it appears improbable that our general conclusions would have been materially affected. Surface temperatures were taken with a radiometer and rectal temperatures with a thermocouple.

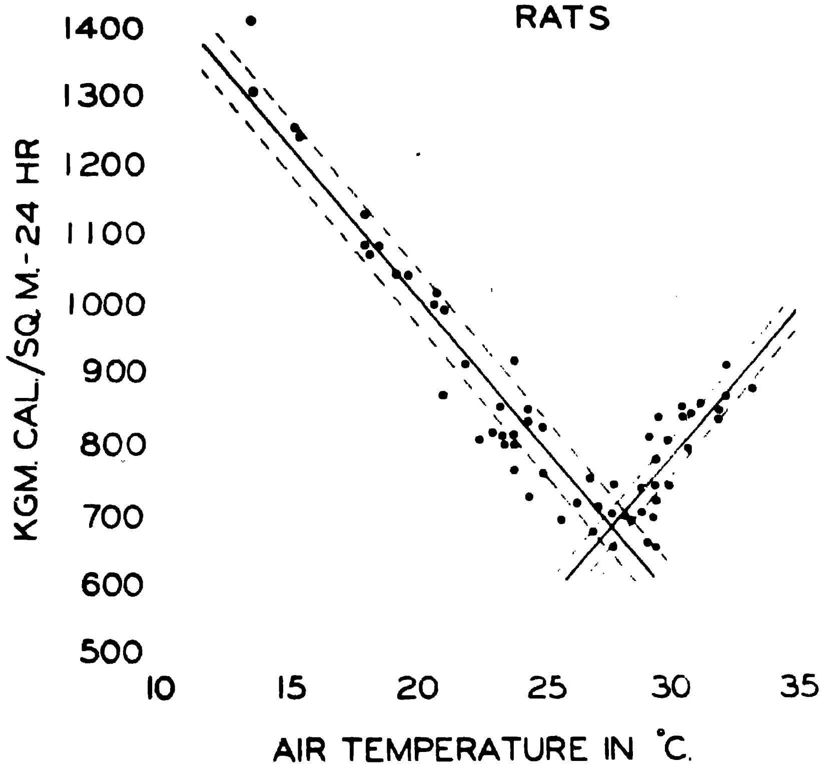

FIG. 1. Standard metabolism of albino rats at various temperatures. Each point represents the mean of 10 animals.

Results

The principal results showing the effect of environmental temperature on heat production can be seen in Figs. 1, 2, and 3.

The marked effect of temperature on the heat production of all three species and the essentially linear increase below the approximate area of thermal neutrality are apparent. These increases in heat production with decreasing environmental temperature may be expressed by the following equations:

(1) $\text{Cal}/M^2/24\ \text{hrs} = 1879 - 43.2T$ (°C) (Rats—below 28.9°)
Standard error of estimate ±23.9.

(2) $\text{Cal}/M^2/24\ \text{hrs} = 2093 - 46.3T$ (°C) (Mice—below 30.6°)
Standard error of estimate ±35.4.

(3) $\text{Cal}/M^2/24\ \text{hrs} = 1426 - 26.1T$ (°C) (Guinea pigs—below 30.0°)
Standard error of estimate ±46.9.

The greater variability of results and the short range available above the critical temperature areas prevented the accumulation of equally reliable data in the hot region. In only one instance have the data justified a fit in this range.

(4) Cal/M^2/24 hrs $= -503 + 42.8T$ (°C) (Rats—above 29.2°)
Standard error of estimate ±15.5.

These data have been used to determine the temperature intervals of minimal metabolism for the three species by smoothing both the test temperature series and heat production values with a moving average of three.

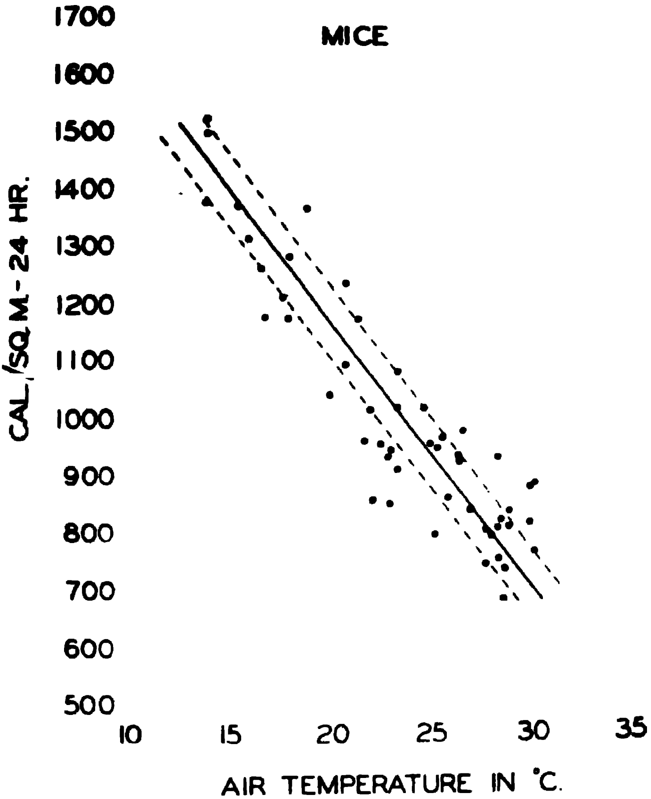

FIG. 2. Standard metabolism of mice at various temperatures. Each point represents the mean of 50 animals.

Inspection of these smoothed values indicated minimal heat production for rats and guinea pigs between 28.0-28.9 and 30.0-30.9°, respectively. The minimal point for mice is not clearly indicated because of the absence of data in the 31° interval. It seems certain, however, that the critical point is above 30° and under 33°, and it is likely that the 31-31.9° interval is the best estimate of its location. With the foregoing reservation in mind, it may be concluded that 28.5°, 30.5°, and 31.5°, are temperature points which are acceptable as conditions of thermal neutrality for rats, guinea pigs, and mice, when normal activity is allowed. Under these conditions metabolisms of the order of 680, 590, and 740 Calories per square meter per 24 hours, in this same species order, are found when surface area is computed as described earlier. The critical temperatures indicated by these data are in rough agreement with those cited by Benedict (1938)[1] for rats and mice; the critical temperature for guinea pigs is, however, definitely higher in this study.

Physical Factors in Temperature Regulation

The most conspicuous point bearing on the comparative temperature regulation of the three species (see Figs. 1, 2, and 3) is obtained from the slopes of the lines on the cold side of the zone of thermal neutrality. For a standard decrease of 1° in environmental temperature, the metabolic increases in Calories per square meter per 24 hours are 46.3, 43.2, and 26.1, for mice, rats, and guinea pigs, respectively. From a biophysical standpoint the relative Calorie cost of maintaining a constant internal body temperature for animals of similar pattern, efficient internal circulation, and comparable peripheral insulation, should be proportional to the ratio of surface area to body volume, or its approximate, body weight. In the present case, the mean weights of 27.1, 351, and 629 grams for mice, rats, and guinea pigs, respectively, indicate, on the basis of surface area formulas previously cited, .299, .129, and .105 square meter per kilogram of body weight. If the increase in heat production per unit of temperature change were solely a function of the relatively greater surface of the smaller species, the observed increase for each species for 1° of environmental cooling should be proportional to its surface-weight ratio. Actually, we find the relative surface-weight ratios for guinea pig, rat, and mouse to

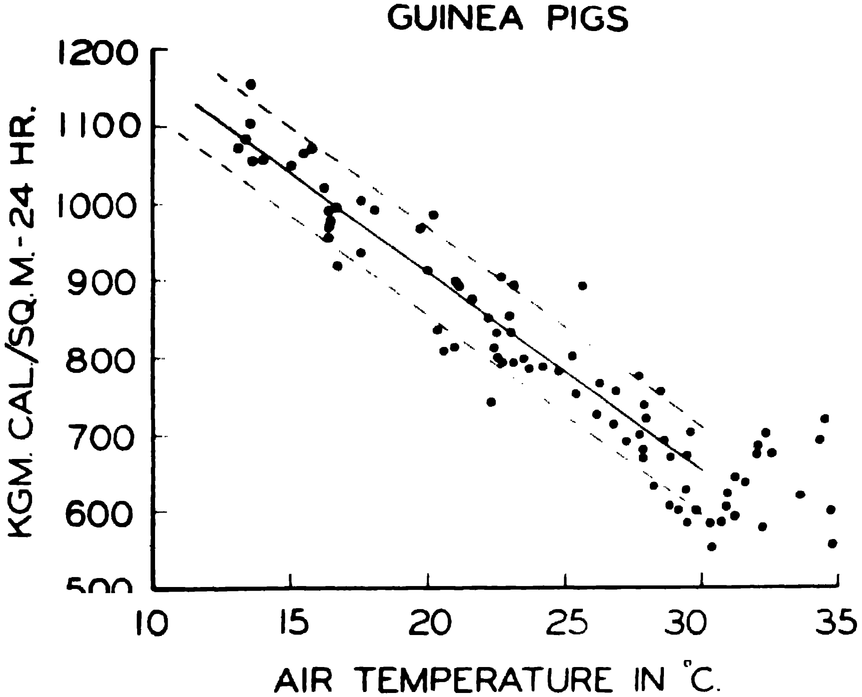

FIG. 3. Standard metabolism of guinea pigs at various temperatures. Each point represents the mean of 6 animals.

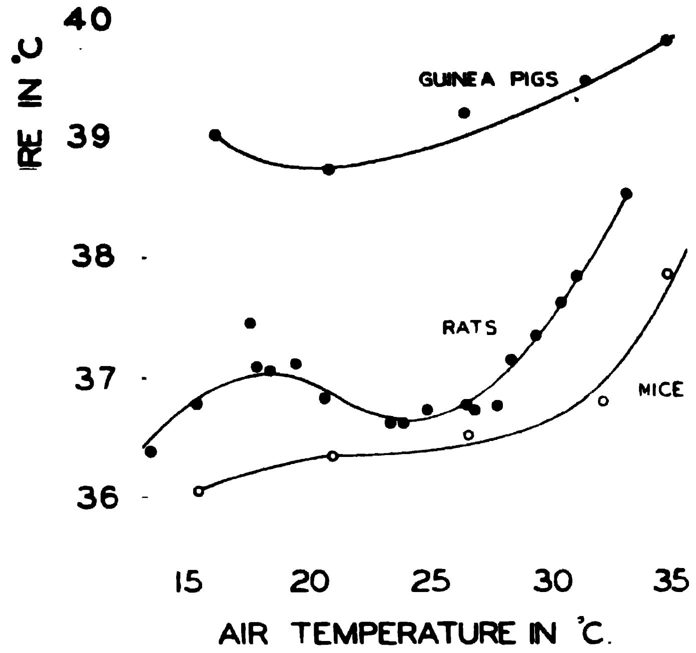

FIG. 4. Rectal temperatures of guinea pigs, rats, and mice. Each point represents the mean of 10 animals.

be 1, 1.23, and 2.81; the ratios of the heat increases (in the same order) 1, 1.66, and 1.77. In a rough sense the conception that the Calorie cost of maintaining a constant body temperature increases with decreasing size is borne out by the order of these two sets of ratios.

Since we wish to consider these metabolic reactions to temperature in relation to heat-loss factors, measurements of rectal temperature and surface temperature

Table 1. Conductance Values at 26.7 °C.

	Guinea Pigs	Rats	Mice
Surface Temperature	31.1° ± 1.2°†	30.8° ± 1.6°	31.2° ± 1.9°
Rectal Temperature	39.2° ± 0.7°	36.7° ± 0.9°	36.5° ± 1.3°
Metabolism*	736 ± 47	727 ± 24	859 ± 35
Metabolism-Evaporation	626	618	720
	Temperature difference (°C)		
Surface-Air	4.4°	4.1°	4.5°
Rectal-Surface	8.1°	5.9°	5.3°
Rectal-Air	12.5°	10.0°	9.8°
	Conductance Cal/M^2/24 hrs/°C		
Surface-Air	142.3	150.7	162.2
Rectal-Surface	90.9	123.2	162.1
Rectal-Air	55.3	67.9	81.0

*Metabolism and evaporation in kg cal/M^2/24 hours.

†Standard deviation.

(radiometric) have been secured, and the important thermal conductances computed. In Fig. 4 are shown the results for rectal temperature. Each point represents 20 measurements at standard depths of insertion. The conspicuous fact here is the wide species range in rectal temperature and the greater stability both in the hot and cold regions of the larger animal. The absolute size factor is, roughly, 1, 10, and 20, for the average mouse, rat, and guinea pig, respectively.

In Table 1 are presented the results of a heat partition at 26.7 °C based on 20 animals of each species. It may be noted that in spite of an advantage of 123 Calories in heat production, the mouse is able to maintain a rectal-air difference of only 9.8° as compared with 12.5° for the guinea pig. If the internal conductance is computed by dividing the heat production by the rectal surface difference, it is seen that the conductance of the mouse is 80 per cent greater than that of the guinea pig. External conductances show only slight species differences, indicating that these animals are similar bodies from the standpoint of heat loss by radiation and convection.

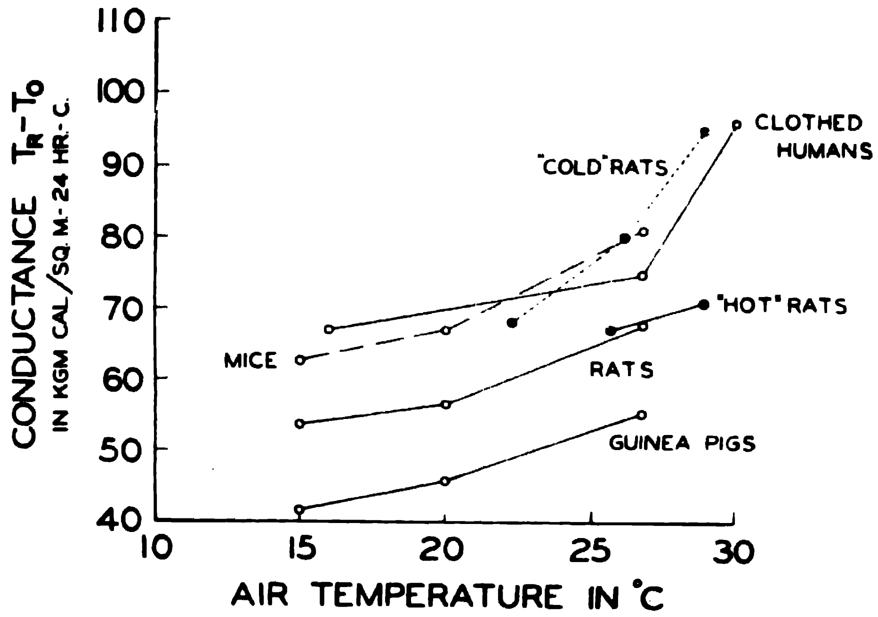

FIG. 5. Overall thermal conductance, rectum to air, for various groups of animals and clothed humans. T_0 is defined as $T_A - \dfrac{E}{K_{T_{SUR}-T_A}}$.

In Fig. 5 are plotted the overall conductances from rectum to air for the three species raised at 24°, for rats raised at 17°-19° (cold) and 31°-32° (hot), and for clothed humans. As might be expected, the mouse has the highest conductance, the guinea pig the lowest. Plump rats raised in a warm environment are better insulated than their "cold" cousins who are notably lean and small as a result of retarded growth. It is interesting to note that normally clothed human subjects have a conductance approximating that of the mouse. From the standpoint of heat regulation, however, this equivalent conductance is maintained in the human *without* any significant increase in metabolism. It is obvious that these conductance comparisons would be greatly improved if restricted to internal conductances expressed in terms of a gradient depth. The practical difficulties are great; it is possible, however, that further rationalization might be possible through expression in terms of some function of a body dimension.

Although conductances decrease for all three animal species as lower air temperatures are reached, it seems probable that vasomotor factors are not principally concerned, but that the decrease means simply that the increase in heat production is slower than the increase in surface-rectal temperature difference, a circumstance which indicates a progressive lowering of average body temperature. Estimates of this decrease in average body temperature in the guinea pig at 10 °C as compared with 26.7° are of the order of 3 to 5°, the exact value depending upon the relative weights assigned to skin and rectal temperatures.

Summary

The present study was undertaken with the aim of providing, for our own laboratory convenience, a set of standards for the common laboratory animals detailing the levels of heat production, body temperature, and thermal conductance which could be expected at various temperature levels. With physical heat loss factors a point of interest, the expression of heat production on a surface area basis was clearly indicated. Formulas were selected for the estimation of surface whose constants appeared to be as satisfactory as any that have been determined for the rational two-thirds power of the weight function.

The results obtained have shown areas of thermal neutrality which are in substantial agreement with previous information on the three species. Below this area, however, there is a linear increase in heat production with decreasing temperature, and the rate of increase is species-specific. The greater rate of increase in the smaller animals is only partially accounted for by a larger relative surface, and it seems probable that variations in peripheral insulation (which are clearly shown in conductance measurements) are very important in distorting the simple association between surface area and heat production which has so often appealed to biologists as a necessary relationship, not only at these lowered temperatures but in the area of thermal neutrality as well.

The increase in heat production at lower temperatures is never sufficient to compensate fully for the increased heat loss, and lower average body temperatures must occur in all three species. This is true in spite of the existence at moderately lowered temperatures of a metabolic reserve potentially capable of restoring average body temperature.

Determinations of surface temperature, heat production and evaporation have permitted the computation of coefficients of external heat loss by radiation and convection. The values found, while slightly larger than those found for resting humans (activity factor) do not vary greatly for the three species in spite of a factor as great as 20 in absolute size.

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The Effects Upon Dogs of Low Oxygen Tensions Combined with Low Temperatures

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The complexity of the stimuli to which living organisms are subjected is nowhere more evident than in high altitudes. While the chief determinant in the external environment there is apt to be the reduced partial pressure of oxygen, various other factors taken together may at times outweigh it in influence. Low air density restricts the flight of birds, intense sunlight requires protective measures, sparsity of food lowers the population density of plants and animals, and low temperatures coupled with wide diurnal changes render difficult the maintenance of homeostasis, particularly so since centers responsible for temperature regulation may be handicapped by lack of oxygen. On account of the interdependence of these two functions, oxygen supply and temperature regulation, a study has been made of the response of dogs to low partial pressures of oxygen in a cold room. The response of the dog to these stimuli may be expected to be influenced by the fact that his respiratory centers are accustomed to serve dual roles simultaneously: gas exchange and heat dissipation.

Methods

Each of four dogs was trained to lie quietly on a piece of tennis net while air was supplied through a Cellophane helmet. Observations were made on pulse rate, respiratory rate and volume, oxygen consumption, and rectal and skin temperatures. Samples of blood were drawn at intervals from the femoral artery and less frequently from the right heart.

The gas mixtures, prepared and stored in standard steel pressure cylinders, were precisely analyzed. The gas was passed through (1) a pressure reducing valve, (2) a wet meter, (3) a two-way cock opening to the air or to (4) a collapsible bag of about two liters' capacity connected to (5) a flutter valve, (6) a tube in the Cellophane mask placed in line with the dog's muzzle, (7) a tube opening from that part of the mask covering the occipital area, (8) another flutter valve, (9) a two-way cock leading to (10) a gasometer of 500 liters' capacity, or to (11) a rubber bag of two liters' capacity. The gas cylinders, gas meter and gasometer were in a room adjoining the low-temperature room, not only for the comfort of one observer but also because the gas meter did not operate accurately below 10 °C. The gas flow was adjusted at a rate considerably in excess of the dog's requirement, bag 4 acting as a buffer between the constantly flowing gas from the cylinder and the periodic inspiration by the dog. The effluent gas was measured at intervals in the gasometer and samples were taken for analysis. Equality of inflow and outflow was accepted as proof of tight connections, proper account having been taken of the R. Q. The only likely source of a leak was around the helmet. By means of sponge rubber smeared with Vaseline, such leaks were eliminated except when struggling loosened the helmet.

On occasions between measurements of metabolism, estimates were made of tidal air. This was accomplished by manually operating simultaneously at the end of expiration cocks 3 and 9. After from two to five breaths, depending on the tidal volume, the cocks were reversed. The air inspired during these breaths was drawn by the dog from bag 4. Exhaled air was collected in bag 9; subsequently its volume was measured with a brass syringe of 350 cc capacity. The volume of air rebreathed under such circumstances had a negligible effect on tidal volume, for when the dog was in a steady state, consistent measures of tidal air could be obtained by this method, using any number of breaths up to five.

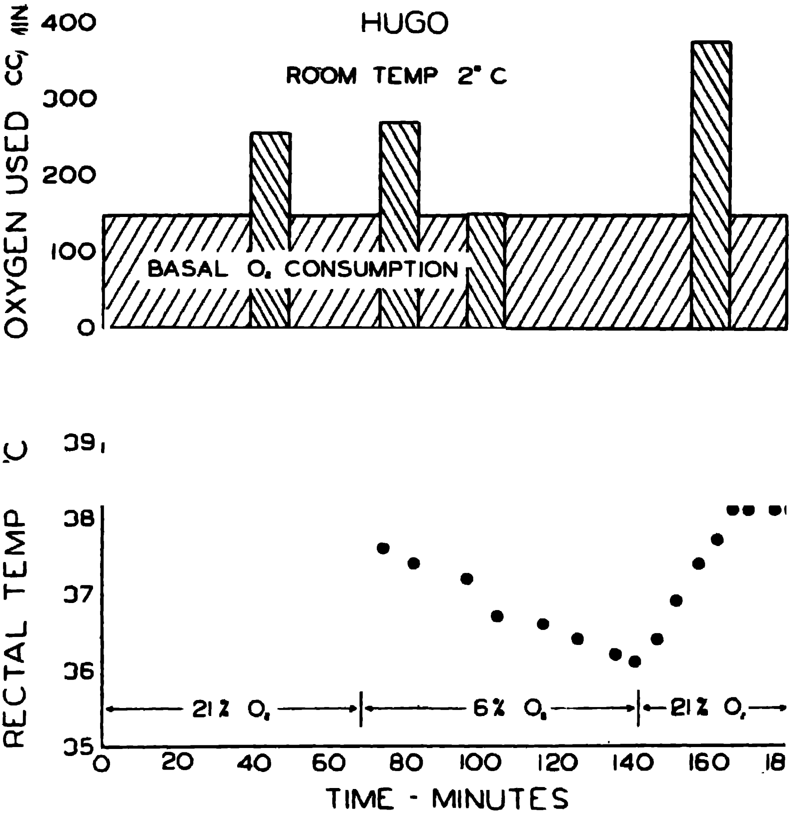

Fig. 1.

Rectal temperatures were determined with a clinical thermometer and skin temperatures with the type of thermocouple used by Aldrich.[1] Five areas were selected: thigh, belly, back, inside an ear flap, and paw.

Arterial blood was drawn without exposure to air and mixed with heparin under oil. Lactate was determined by Edwards' method[2] on 0.5 cc, sugar by the micromethod of Folin and Malmros,[3] and CO_2 and O_2 content on the Van Slyke apparatus, using the combined method on 0.5-cc samples. About 3 cc was equilibrated at body temperature to determine O_2 and CO_2 capacities. These determinations permit calculation of pCO_2, pH, and percentage saturation with oxygen.[4] In preliminary experiments oxygen dissociation curves at 34, 37, and 40 °C and at pH values of 7.1, 7.3, and 7.5 were determined. From these it was possible to calculate

pO_2 of the blood. On those occasions when both arterial and mixed venous blood were drawn during a measurement of metabolism, we were able to calculate oxygen utilization and cardiac output.

In an early experiment a pneumothorax developed after puncture of the right heart. We have not previously observed this under ordinary conditions and are inclined to attribute the accident to faulty technic plus the complications of increased respiratory and circulatory activity. In subsequent experiments puncture of the right heart was usually postponed to the last part of the experiment.

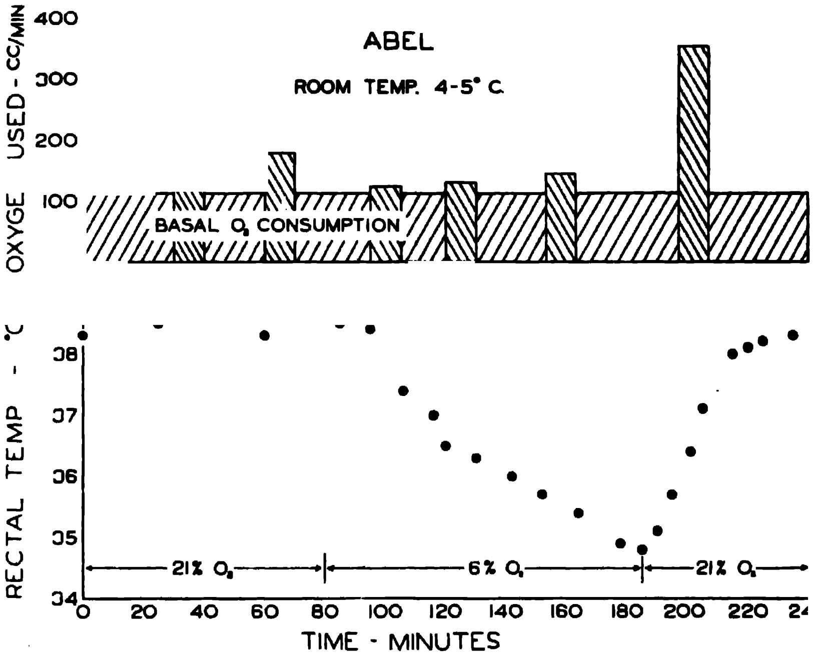

FIG. 2.

The dogs used as subjects were Hugo, a young male of the Bassett hound type; Abel, a male wire-haired terrier sympathectomized four years before and described by Brouha, Cannon and Dill;[5] Puppy, a young male mongrel; and Speedwell, a mature male greyhound. They were all in good health and, aside from Abel, had undergone no operative procedures. The first three had oxygen-combining capacities of from 23 to 25 volumes per cent, and the greyhound, about 30 volumes per cent. Despite this apparent advantage, the greyhound was the least resistant subject.

Results

Figs. 1 and 2 illustrate the changes in rectal temperature and in oxygen consumption in experiments on Hugo and Abel. While the dog was in the cold room breathing normal air the oxygen consumption usually was elevated one-half or more above the basal level as measured in a room at about 20 °C. Soon after the shift to low oxygen, the oxygen consumption decreased nearly or quite to the basal level. When normal air was supplied, the rate of oxygen consumption increased rapidly to about three times the basal level. The rectal temperature remained constant, or nearly so, so long as normal air was breathed, but fell in a roughly linear fashion at the rate of about 2 °C per hour throughout the period of oxygen lack. The rate of return to normal was about three times as rapid.

An experiment of longer duration on Hugo is described in Fig. 3. Here the metabolism sank somewhat below the basal level in three cases and again increased to about three times the basal level in recovery. It is to be expected that, so long as shivering or other bodily movements do not occur, the basal oxygen consumption will fall with falling temperature. We shall return to this question later. The decline in rectal temperature was at the rate of 2 °C per hour during the first hour of exposure to low oxygen, but flattened out to 0.5 °C per hour during the last hour. A rectal temperature of 34 °C was reached after five hours' exposure to 6 per cent oxygen (roughly equivalent to the summit of Everest) and to a temperature of from 3 to 5 °C. Before discussing these results, we shall present observations on the properties of the blood and on circulatory changes.

Tables 1 and 2 compare in Abel and Hugo the composition of arterial and venous blood (from the right heart) during exposure to cold air of normal composition and to cold air containing 6 per cent oxygen. In cold air the values for arterial blood are like those observed under ordinary conditions. Hugo, the normal dog, has somewhat less than the usual oxygen utilization, while Abel has an unusually large utilization. Exposure to low oxygen increased blood lactate about four times and reduced the total CO_2 content about 10 vol. per cent. Yet the pH was more alkaline than usual. In other words, the partial pressure of CO_2 was lowered more than the combined CO_2. Arterial saturation dropped to about one-third capacity and partial pressure of oxygen was reduced to 20 mm or less. The changes in venous blood ran parallel to those seen in arterial, although the utilization of oxygen was less than before. In Abel the extraordinarily low value of 11 per cent saturation was reached. The estimated cardiac outputs in normal air and in low oxygen are, respectively, for Abel 1.9 and 2.3 and for Hugo 6.4 and 4.2 liters per minute. Since the heart rate approximately doubled, it follows that the stroke volume was cut in half in the case of Abel and reduced by three-quarters in the case of Hugo.

Table 1.

ABEL: Breathing Air at 8 °C
Rectal temp. = 38.6 °C. Lactate = 1.1

	Arterial	Venous	Δ
CO_2 content	38.7	46.4	7.7
O_2 content	22.4	12.8	9.6
pCO_2	38	50	12
pO_2	90	36	54
% HbO_2	96	55	41
pH	7.34	7.30	0.04

After Breathing 6% O_2 at 5 °C for 100 min
Rectal temp. = 34.9 °C Lactate = 4.4

CO_2 content	26.5	30.9	4.4
O_2 content	8.3	2.6	5.7
pCO_2	19	24	5
pO_2	16	9	7
% HbO_2	34	11	23
pH	7.49	7.46	0.03

Table 2.

HUGO: Breathing Air at 5 °C
Rectal temp. = 38.7 °C Lactate = 1.2

	Arterial	Venous	Δ
CO_2 content	41.9	44.6	2.7
O_2 content	22.8	18.7	4.1
pCO_2	40	44	4
pO_2	78	47	31
% HbO_2	94	77	17
pH	7.38	7.37	0.01

After Breathing 6% O_2 at 2 °C for 120 min
Rectal temp. = 36.5 °C Lactate = 6.5

CO_2 content	31.3	33.7	2.4
O_2 content	9.3	5.7	3.6
pCO_2	24	27	3
pO_2	20	15	5
% HbO_2	38	23	15
pH	7.45	7.44	0.01

The course of blood lactate and arterial pH throughout an experiment is seen in Fig. 3. Blood becomes alkaline at once and returns slowly toward normal as time goes on, to become abruptly acid when normal air is admitted. Lactate rises slowly to a plateau and remains undiminished in the first minutes of recovery. Throughout the experiment, arterial saturation remained between 29 and 36 per cent and arterial pO_2 between 15 and 19 mm. When normal air was turned on, the arterial saturation rose to 87 per cent and the pO_2 to 50 mm. It will be noted that these values are considerably below the initial values (Tables 1 and 2) despite the fact that a reduction from 37 to 34 °C increases the saturation of hemoglobin at pH 7.4 and at pO_2 50 mm from 85 to 91 per cent.

There is an interdependence between the arterial pH and the blood lactate concentration, but an even closer interdependence between arterial pH and respiratory function. It is common to speak of the respiratory changes as being caused by pH changes, the more acid the blood the greater the respiratory response; but in this instance we see considerable increases in respiratory volume and rate, associated with a considerable alkalosis. For example, in the experiment on Hugo, partly described in Fig. 3, the respiratory rate, though subject to wide fluctuations, remained within the range of 40 to 90 per minute, while the respiratory volume increased from about 6 liters per minute to from 10 to 20 liters per minute. Since the metabolic rate decreased nearly one-half at the same time, it follows that the alveolar ventilation was more than doubled. The confirmation of this conclusion is seen in Tables 1 and 2: the arterial pCO_2 is approximately cut in half.

Finney, Dworkin and Cassidy [6] found R. Q. values as low as 0.43 in dogs treated with insulin and cooled to 26 °C. Within the narrower range of temperatures covered in our experiments the R. Q. did not fall below the usual limits.

Discussion

Simultaneously exposing dogs to low oxygen and low temperature at once upsets temperature regulation. This had remained fully adequate in the cold room, so long as normal air was breathed, in part as a result of vasoconstriction, as is seen by the low skin temperature, but chiefly as a result of the increase in heat production associated with shivering. Soon after low oxygen was admitted, shivering became intermittent and usually ceased entirely. There was a further fall in skin

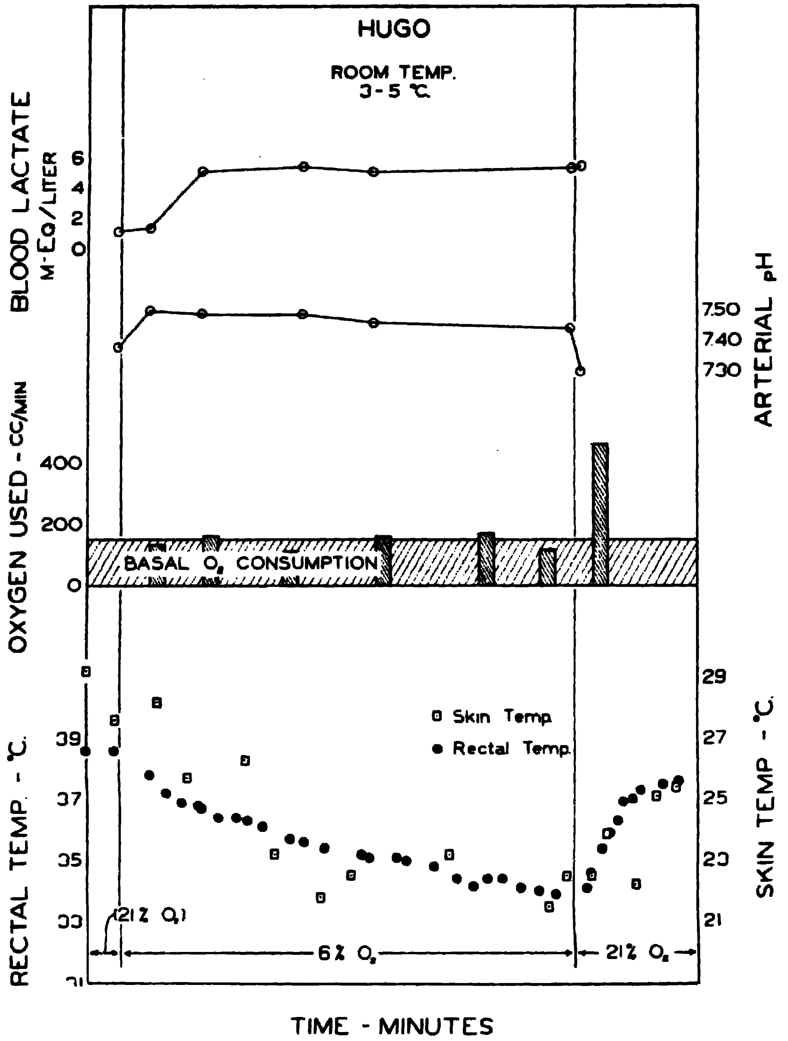

Fig. 3.

temperature, but this did not greatly exceed the rate at which rectal temperature decreased. The failure of temperature regulation, despite the reduction in radiation and convection, clearly depends on inhibition of shivering and the associated decline in heat production. The dependence of shivering on oxygen supply was demonstrated by the response of the dogs when the gas mixture was replaced by air; for example, in the experiment described in Fig. 3, very violent shivering began within 45 seconds. Evidently a temperature as low as 34 °C did not in itself inhibit shivering.

In studies of homeostasis McDonough[7] found that normal and sympathectomized dogs withstood 6-per cent oxygen equally well, and that even in 4-per cent oxygen the resistance of the sympathectomized dogs was not greatly reduced. We therefore paid particular attention to the responses of Abel (one of the dogs used in her experiments) as compared with those of the other three dogs. Of the four dogs studied, his temperature fell most rapidly under similar conditions, but we are inclined to attribute that to the poor protection afforded by his thin wiry hair. His respiratory response was like that of the other dogs. His circulation was the least adequate, as judged by cardiac output and oxygen utilization. Although this may depend on sympathectomy, other dogs must be tested before this phenomenon can be accepted as characteristic.

Both the production of an alkalosis and the accumulation of lactic acid in dogs exposed to low oxygen would ordinarily be attributed directly to the effects of oxygen lack. It is not certain, however, that this is correct. Anrep and Cannon,[8] and later Bock, Dill and Edwards,[9] showed that dogs made alkaline by ingestion of sodium bicarbonate respond by accumulating lactic acid. In degrees of anoxemia as great as man can withstand there is alkalosis only in the early stages of acclimatization. No accumulation of lactic acid was observed either by Bock, Dill and Edwards [9] or later in high altitudes by Edwards.[10] It is possible that the dog is more tolerant of alkalosis than man, since in severe panting his blood may reach a pH of 7.6.[11] On this account the respiratory stimulus from oxygen lack may meet in the dog less inhibition from loss of CO_2 than in man. During long exposure to low oxygen our dogs maintained a large respiratory volume without periods of apnea such as are seen in man. It appears that the dog in anoxia tolerates a greater and more sustained alkalosis than man and the observed accumulation of lactic acid may depend directly on this and only indirectly on lack of oxygen. The accumulation of lactic acid to an equilibrium level gains within a few minutes the same end as the reduction in alkaline reserve attained by other means over a period of days in man.

It seems likely that the superiority of the dog in respect to capacity to withstand low oxygen, as witnessed by his survival at an altitude equivalent to the top of Everest for 5 hours, depends in part on his tolerance of alkalosis, his facility in reducing alkaline reserve, and the associated early attainment of relatively high alveolar oxygen tensions. In addition to this, his brain must be unusually resistant to oxygen deprivation. Man usually collapses when the partial pressure of oxygen in arterial blood drops below 25 mm Hg, but our dogs withstood values as low as 15 mm.

It must be emphasized that signs of circulatory and of respiratory failure were seen in some of these experiments. Upon admission of air, arterial blood did not always increase at once to its usual value. When the experiments were concluded, the dogs appeared to be dizzy, but, with the exception of one dog that received a pneumothorax during a cardiac puncture, all recovered rapidly. The dogs appeared to be only semiconscious during much of the time; occasional sudden bursts of violent struggling were followed at once by a marked increase in cyanosis. When struggling occurred it sometimes forced an early termination of the experiment because of respiratory and circulatory collapse.

The inhibition of shivering seen in these experiments is not a new phenomenon. Richet [12] notes that asphyxia prevents shivering, and it appears that any major disturbance of metabolic processes in the brain may act similarly. The insulin shock treatment of schizophrenia is associated with lowered body temperature, according to Sakel;[13] the temperature rises only when glucose is administered. Cassidy, Dworkin and Finney [14] were able to lower the temperature of dogs or cats to 25° without shivering by insulin injections.

Anesthesia prevents shivering and makes possible the lowering of body temperature of man to 27 °C, as shown by Fay and Smith.[15] In acute alcoholism, body temperatures as low as 24 °C have been observed without fatal issue;[16] presumably, alcohol not only causes vasodilatation, but also inhibits shivering. Finally, in a state of physical exhaustion, such as is seen in men lost in blizzards, shivering may cease and death from freezing may occur.

The decrease in body temperature for a given degree of oxygen lack is most rapid in small animals, as has been shown by Gellhorn.[17] Mayer and associates[18] have demonstrated a parallelism between decrease in oxygen consumption and in oxygen tension in animals exposed for one hour to various atmospheres. In our opinion there is no evidence of a direct dependence of oxygen consumption on oxygen tension in mammals. Rather, it seems likely that body temperature decline depends on inhibition of shivering and possibly in some instances on disturbances of vasomotor regulation. Decline in oxygen consumption is probably dependent on decline in temperature. Whatever the chain of events, the temporary advantage gained by small over large organisms in low oxygen at low temperatures is clear. For example, Gellhorn[17] has found that mice survive for 10 minutes an oxygen concentration at low temperatures that proves fatal at 37° within the same length of time. Guinea pigs show less adaptability to low oxygen in low temperatures. It must be emphasized, however, that muscular activity is not compatible with survival under such conditions; the animal is in an unstable state in which on the one hand a sudden demand for energy transformation may cause collapse (as in our struggling dogs) or on the other hand a temperature low enough in itself to cause death may be reached.

Conclusions

Subjecting dogs to 6-per cent oxygen in a cold room resulted in inhibition of shivering and decrease in body temperature. As soon as atmospheric air was supplied, violent shivering began and body temperature rose.

The resistance of dogs to low oxygen was associated with their tolerance of alkalosis, their accumulation of lactic acid, and the toughness of their nervous system. They remained semiconscious with low metabolism and normal R. Q. as long as they were quiet; struggling induced circulatory and respiratory collapse and increase in R. Q. Their state was an unstable one; death was imminent during a sudden struggle on the one hand, or from too great reduction of essential metabolic processes by low temperatures on the other.

Discussion

Alan C. Burton: Any discussion I could add would be of Dill's paper. Doctor Bronk and I found, using the action currents of the muscles of the cat as a sensitive index of shivering and 'thermal muscular tone,' that inhibition very promptly followed the substitution of nitrogen for air. We also noted an enhancement of the muscle activity when air was once more given, in that the frequency of contraction of individual muscle units reached a higher value than was normally seen.

The inhibition of shivering by oxygen lack may be perhaps regarded as an interesting example of the suppression of one physiological function in the interests of a more vital function in circumstances of crisis.

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Temperature Factors in Animal Production[1]

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This paper discusses some temperature factors which influence productive level and maintenance cost and consequently productive efficiency of farm animals.

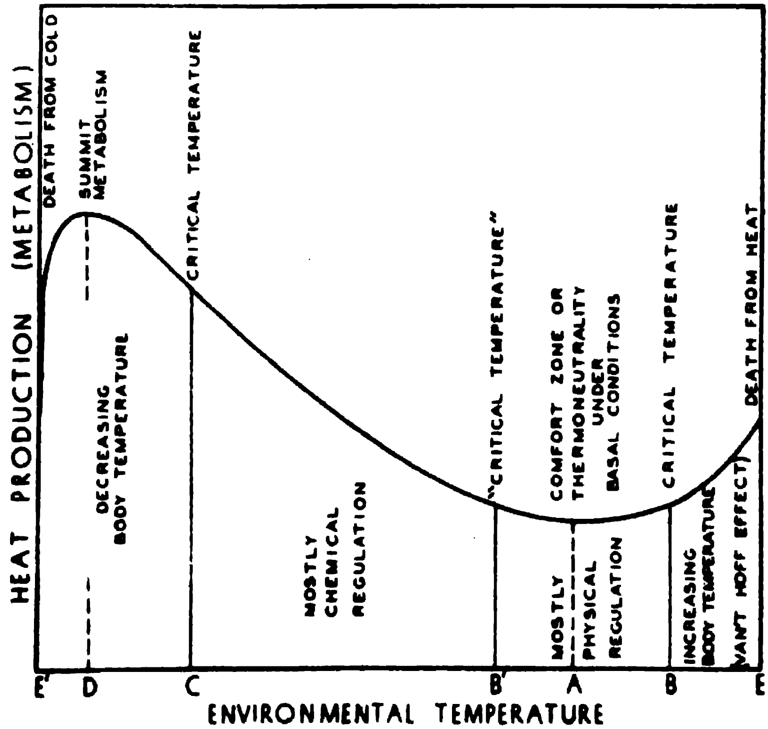


FIG. 1. Diagram of the influence of environmental temperature on heat production and body temperature.

1. Influence of Environmental Temperature on Heat Production and Maintenance Cost in Animals

In Fig. 1, modeled after Giaja, environmental temperature *A* represents thermal neutrality, at which heat production is minimal. This neutral temperature is probably not a point but a zone. The temperature segment *B*−*B'* includes this zone of thermoneutrality and also the adjacent environmental temperatures at which the body temperature is regulated, not by changes in the rate of heat production (maintenance cost), but by physical methods which will be presently enumerated. Incidentally, the segment $B-B'$ includes the ventilating engineers' comfort zone, the exact position of which depends on the relative humidity and air movement.

Temperature B', at which heat production begins to increase measurably in order to balance the increased heat outgo resulting from lowering of the environmental temperature, is referred to by animal husbandmen as the "critical temperature," because at this temperature the maintenance cost begins to rise. This may be a matter of economic importance. Actually it is not known whether it is of economic importance, because the "critical temperatures" reported by calorimetric laboratories were not obtained under practical, that is economic, conditions of animal production, but under very special conditions of fast (R. Q. near 0.7), complete rest, given humidity and air movement, given insulation of fur or feathers, given subcutaneous fat, and acclimatization to a given environmental temperature. The critical temperatures under practical conditions of management on the farm are unknown, and, as will be presently illustrated, probably have little relation to the laboratory findings.

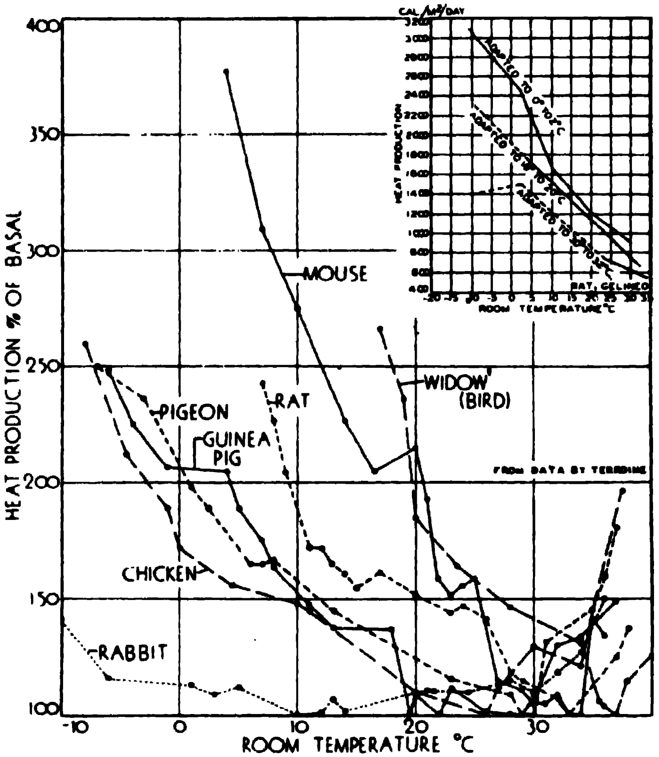


Fig. 2. Influence of environmental temperature on heat production of animals expressed as percentages of the minimum heat production.

At environmental temperature C in Fig. 1, the body temperature begins to decline despite its continuously increasing heat production. The temperature-regulating mechanism is not equal to the task confronting it.

Environmental temperature D in Fig. 1 represents the position at which heat

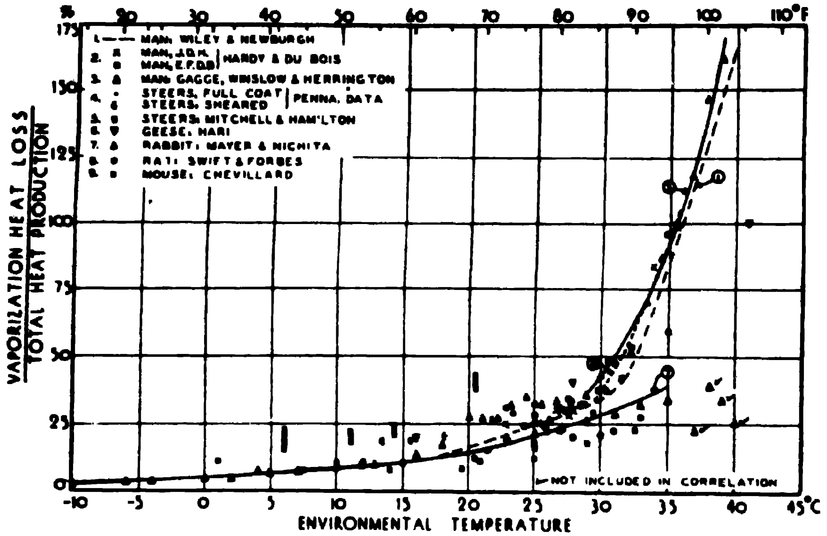


FIG. 3. Influence of environmental temperature on the heat dissipated by vaporization of moisture from skin and respiratory passages plotted on an arithmetic grid.

production is maximal, the summit metabolism of Giaja.[2] Following environmental temperature *D*, the temperature-regulating mechanism begins to break down, and heat production as well as body temperature declines.

On the high-temperature end of the curve there is the "critical temperature" *B*, at which body temperature begins to rise because the heat-regulating mechanisms are not capable of dissipating all the heat produced by the body.

The positions of the critical temperatures vary with (1) the ability of the animal to sweat profusely, (2) the relative humidity and air motion which govern the vaporization rate of the sweat and respiratory-passage moisture, (3) amount and nature of subcutaneous fat and fur or feathers, (4) ratio of heat-dissipating surface to body weight, (5) normal body temperature, and no doubt other factors.

Fig. 2 illustrates factually parts of the diagram in Fig. 1: (1) other conditions being equal, the larger the animal, the flatter its heat-production curve with decreasing environmental temperature; (2) if an animal is acclimatized to a low environmental temperature it produces more heat at higher temperatures than if it is acclimatized to the higher temperature; (3) the environmental-temperature range which animals can withstand on the cold side of thermoneutrality is very much greater than on the hot side. Farm animals especially have powerful methods for protecting themselves against cold, and feeble methods, especially in non-sweating species, for protecting themselves against heat.

2. Relative Effect of Environmental Temperature on Heat Dissipation by Vaporization in Sweating and Non-sweating Species

It is known that as the environmental temperature approaches body temperature, the burden of heat dissipation is shifted from radiation, conduction and convection, to vaporization of moisture from (1) the skin of sweating animals, and (2) the respiratory passages, especially of slightly-sweating animals.

The rise in the percentage heat loss by vaporization with increasing environmental temperature appears to occur in a different manner in profusely sweating species, such as humans, and in slightly sweating species, such as rabbits, rats, mice, cattle, sheep, swine, and poultry. This is illustrated in Fig. 3, plotted on an arithmetic grid, and Fig. 4, plotted on arithlog grids.

In these figures the heat loss by vaporization in sweating man shows an irregular course up to 29 °C (84 °F). Up to that temperature, from 25 to 35 per cent of the heat produced is dissipated by vaporization. At 28-29 °C there is a break in the vaporization curve of man, but not in the rat, mouse or rabbit. From about 29 °C on, the rise in the vaporization curve of man is exponentially continuous, as might be inferred if the Van't Hoff-Arrhenius law[3] were applicable to this phenomenon. The heat dissipation by vaporization rises at the instantaneous rate of 15 to 19 per cent per 1 °C rise in the environmental temperature.

As pointed out by Kuno,[4] the "critical temperature" for sweating in man ranges from 27 to 32 °C (81 to 90 °F), depending on season and on other circumstances, and it is probable that the temperature of the break in the curve shown in Fig. 4 is not a constant, but would vary from 27 to 32 °C.

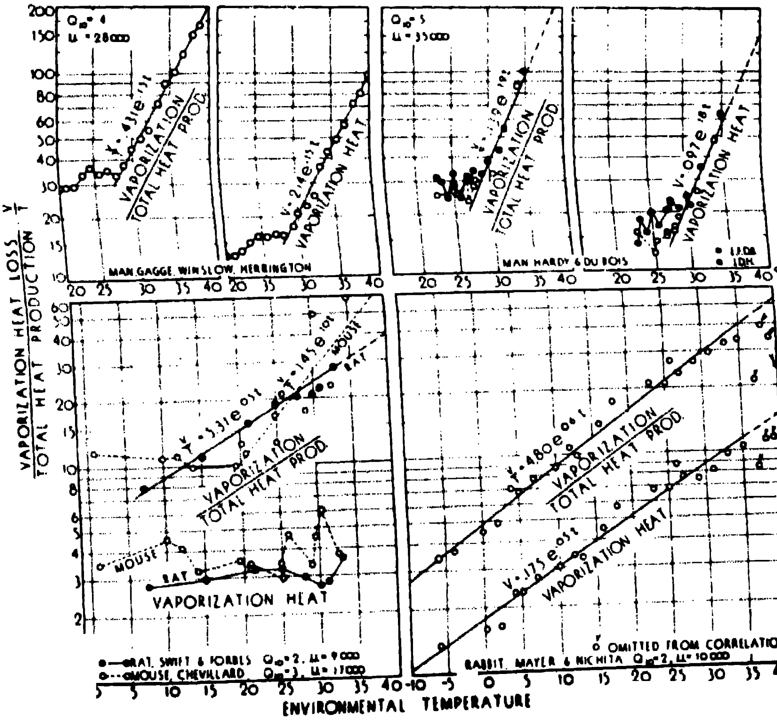


FIG. 4. The data in Fig. 3 are here plotted on arithlog grids.

The curve of rise in heat dissipation by vaporization with increasing temperature is strikingly different in slightly sweating rabbits, rats and mice, and in profusely sweating man, the importance of this difference being that the same may hold true for farm animals which do not appear to sweat, such as cattle, sheep, swine and chickens. The curve of heat dissipation by vaporization rises abruptly at 28 to

29 °C in man but not in the rabbit, rat, and mouse. At 36 °C (97 °F), the heat dissipation by vaporization is 100 per cent of the heat production in man, and only 35 per cent to 60 per cent in the rabbit, rat, and mouse; at 40 °C (104 °F) the heat dissipation is 200 per cent of the heat production in man and less than 35 per cent in the rabbit. The curve of the rat resembles that of the rabbit. The data on the mouse in Fig. 4 are rather irregular, but they seem to show a break at about 25 °C (77 °F), following which the rise in heat production is roughly exponential[3] resembling more closely the curves of rabbit and rat than man.

During the phase of logarithmic rise in the percentage heat dissipation by vaporization, its instantaneous rate of rise per °C is about 10 per cent for the mouse, 5 per cent for the rat, 6 per cent for the rabbit, and 15 to 18 per cent for man.[3] Evidently, as compared to rabbit, rat or mouse, man has a highly sensitive and efficient thermoregulatory mechanism for high environmental temperatures.

Fig. 4 shows an apparent difference between man on the one hand and rat and mouse on the other in the relation between the curves of absolute water vaporization and percentage of heat dissipation by vaporization. In man the two curves are parallel; in the rat and mouse they are not. In the rat, the amount of vaporization is nearly independent of temperature; yet the percentage heat dissipated by vaporization rises because the heat production declines with increasing temperature. This apparent difference may disappear with further accumulation of data.

3. Influence of Environmental Temperature on Cardio-respiratory Activities

The cooling function performed by sweat vaporization in profusely sweating animals is performed in part by increased respiratory-passage vaporization in slightly-sweating animals. This is accomplished by an increase in the respiration rate, often developing into panting, that is, very rapid but shallow respiration. However, panting cannot compensate completely for inability to sweat; as inferred from the fact that in hot environments about $\frac{2}{3}$ of the total vaporization in man is from the skin while only $\frac{1}{3}$ is from the respiratory passages, and as illustrated quantitatively in Figs. 3 to 4 by the differences in heat dissipation by vaporization in man and rabbit, and in Fig. 5 by the differences in the respiration rate, pulse rate, and rectal temperature in a profusely sweating species, man,[5] and a slightly sweating species, the dairy (Jersey) cow.[6] This difference substantiates the fact[7] that non-sweating animals cannot withstand high temperatures even with the increased respiration rate.

Fig. 5 indicates that in cattle the respiration rate is doubled for an increase of 10 °C (18 °F) in the environmental temperature. In man the respiration rate is practically the same throughout the year, tending to decrease with increasing temperature. According to the Van't Hoff law, the speed of a process is doubled for an increase in 10 °C in the reacting system; but in the case of the respiration rate, it is doubled not for an increase in 10 °C in the body, which is the reacting system, but in the environment. How shall one explain this peculiar type of applicability of the Van't Hoff law? It may be that the temperature of the trigger mechanism concerned varies directly with the environmental temperature, even though the temperature of the body as a whole is not changed. The same explanation might be offered for the logarithmic rise in the vaporization rate shown in Figs. 3 and 4.

Fig. 5 also indicates the effect of changing environmental temperature on the pulse rate of sweating and non-sweating species. In the sweating species, the pulse rate rises with increasing environmental temperature, presumably because the blood is shunted from its normal channels to the surface, where it is cooled by the vaporization of sweat. The pulse is increased by way of compensation for the reduction of available blood for O_2 transport. In the non-sweating species, on the other hand, the pulse rate declines with increasing environmental temperature, presumably because in the absence of sweat the skin is not cooled. Therefore the blood may be sent to the interior instead of to the surface.

Finally, as might be expected from Figs. 3 and 4, Fig. 5 shows that the body temperature of non-sweating animals rises more rapidly than that of sweating animals with increasing environmental temperature above 70 °F or 21 °C.

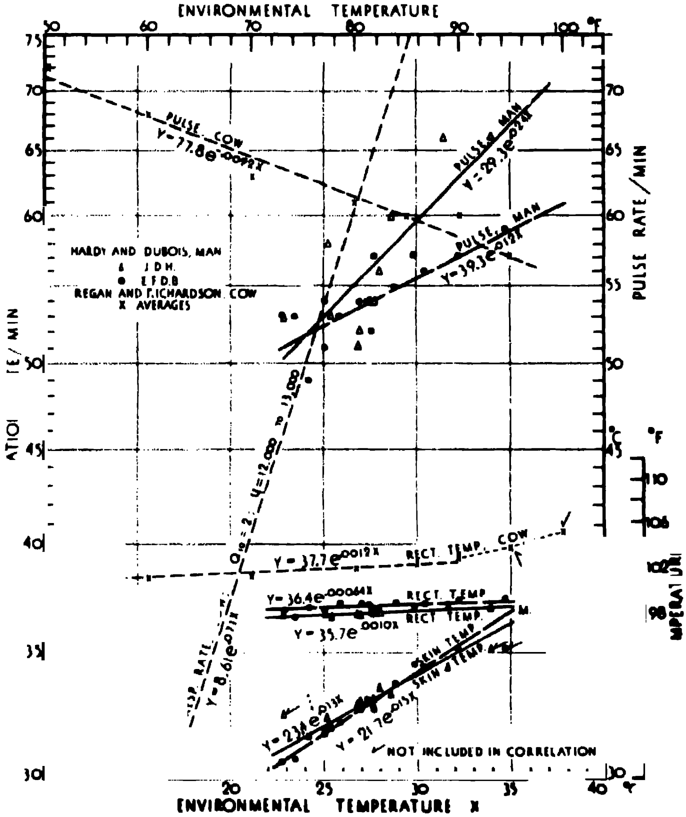


FIG. 5. Comparison of the influence of rising environmental temperature on respiration rate, pulse rate, and rectal temperature in men and cattle.

4. Influence of Environmental Temperature on Productivities and Efficiencies of Farm Animals

a. Effect of Cold Weather on Productivities. It is generally known that farm livestock are wintered without apparent injury on the open range in the severe-winter mountain and northwestern states. Thus the winter temperature at Miles City, Montana, is often −35 °F to −40 °F, yet horses, cattle, and sheep in government experiment stations there are wintered outdoors without injury. Moreover, Dice[8] has recently reported data on dairy cattle kept outdoors at near 0 °F without signs of depression of milk production or increase of maintenance cost.

These reports are not so surprising as may first appear. Farm livestock kept outdoors respond to approaching cold weather by growing warm winter coats of fur or feathers.[9] Thus they develop their own protection against cold and have no urgent need of barn protection. Moreover, incidental to their high productive processes, farm animals consume large quantities of feed. This gives rise to a correspondingly large heat increment of feeding, the so-called specific dynamic action or calorigenic effect, which helps immensely in keeping the animal warm in cold weather, and makes it unnecessary for the body to increase the oxidation of its tissues for maintaining normal body temperature. The heat increment of feeding may be 100 per cent above the basal metabolism. Rapid rise in heat production (maintenance cost) with declining environmental temperatures in fasting and resting animals is no indication that there is a similar rise in normally-fed animals under farm conditions.

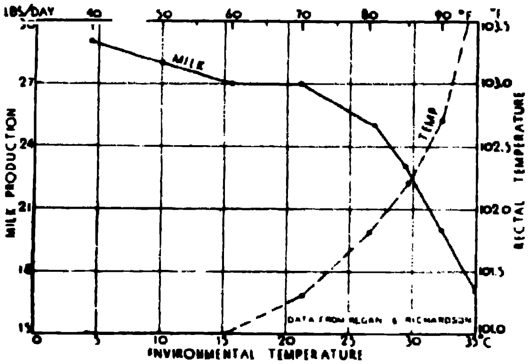


FIG. 6. Influence of environmental temperature on rectal temperature and on milk production in Jersey cattle.

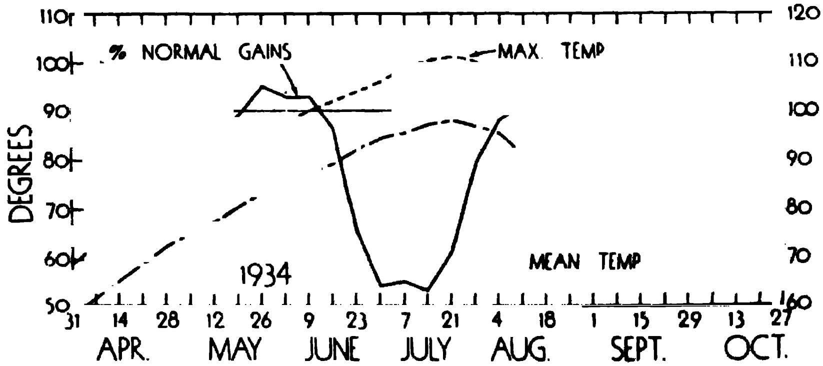
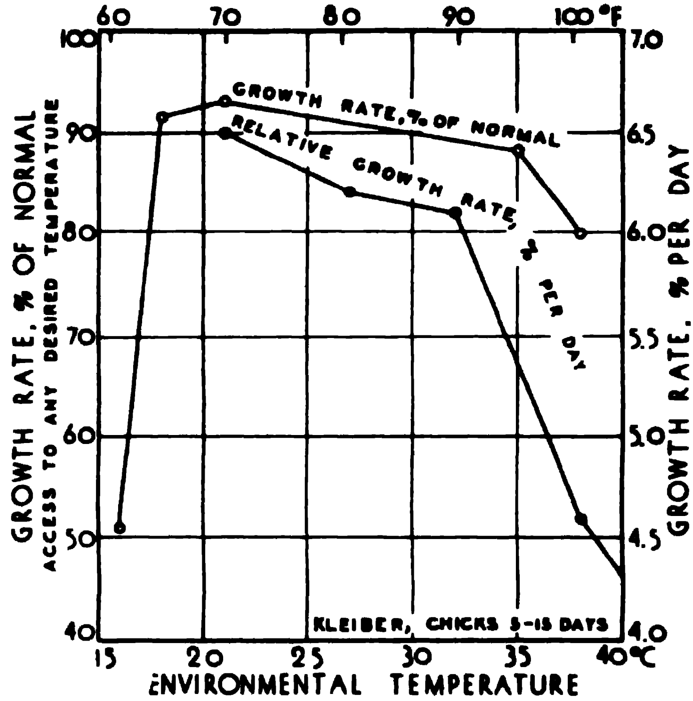


FIG. 7. Influence of environmental temperature on growth of chickens.

The conclusion follows that unless the winter weather declines to 0 °F, simple sheds designed for protection against snow, rain, and wind would meet the animal's need for warmth, and incidentally avoid troublesome ventilation and epidemiological problems. The elaborate and expensive barns currently employed by many dairymen and other animal husbandmen would seem to be superfluous except in the very coldest localities.

b. Effect of Hot Weather on Productivities and Efficiencies of Farm Animals. As previously noted, sweating animals can withstand much higher temperatures than non-sweating animals. In non-sweating animals, at any rate in cattle, the body temperature begins to rise above its normal level when the environmental temperature reaches about 70 °F, or 21 °C. Rise in body temperature is associated with a rapid rise in heat production (maintenance cost), and decline in productivity, as shown in Fig. 6, based on Regan's[10] observations. When the environmental temperature was increased from 60 °F to 95 °F (from about 16 °C to 35 °C), the rectal temperature of the cow was increased from the normal 101 °F level to approximately 104 °F (from 38° to 40 °C), the daily milk yield was reduced from about 27 to about 17 lbs, the casein declined from about 2.1 per cent to about 1.8 per cent, and the solid-not-fat declined from about 8.1 to about 7.6 per cent. The seriousness of the damage of high environmental temperature to milk production is evident from the fact that temperatures of 80 °F to 100 °F are quite common in our richest agricultural regions, especially in the corn belt, where the temperature often rises to 110 °F.



Influence of environmental temperature on growth of chicks in a constant-temperature cabinet.

What was said concerning the depressive influence of high temperature on milk production is also applicable to growth. Thus Fig. 7 shows[11] the precipitate decline in growth of chickens during a hot July in Columbia, Missouri, when the maximum daily temperature rose to 110 °F (43.3 °C), and the mean daily temperature rose to 98 °F (37 °C). Note that the normal body temperature of chickens is not 98 °F, as it is in man and in most mammals on the farm, but 106 °F (41 °C), so that this temperature must have been even more severe on non-sweating mammals.

Fig. 8 shows the influence of environmental temperature on growth of chicks 1 to 2 weeks of age.[12] This growth rate appears maximum at the surprisingly low temperature of 70 °F (21 °C).

It is instructive to note that cattle native to hot countries endure hot environments much better than cattle native to temperate countries—and this may be true of other species. Thus Zebu (or Brahman) cattle, *Bos Indicus*, stand heat better than the European cattle, *Bos Taurus*.[13] This is probably because Indian cattle have more sweat glands than European cattle, just as humans native to hot climates have more sweat glands per unit skin area than natives of cold climates.

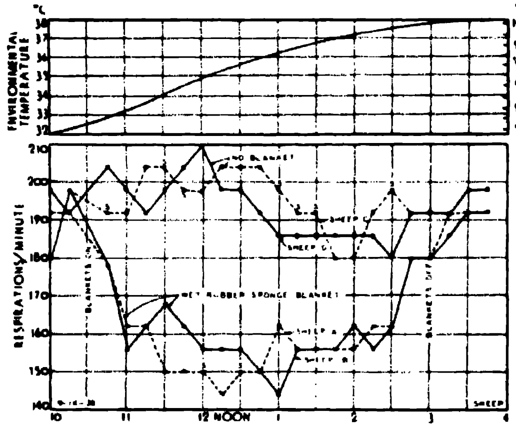


FIG. 9. The influence of a wet sponge-rubber blanket on the respiration rate of sheep.

c. Cooling Non-sweating Animals in Hot Weather. Since overheating in non-sweating animals is due to lack of body-surface moisture for vaporization, the obvious method for cooling would seem to be to apply moisture from the outside. Swine are known to resort to mud wallows to get surface moisture in the desirable form of mud. Cattle prefer to stand in cool water during hot weather, and wild sheep naturally repair to higher altitudes during the hot months.

Under intensive commercial conditions these natural cooling devices have not always been accessible. Many dairymen install powerful fans on the theory that fans cool cows as they do humans. It is obvious from what has been previously said that this theory cannot be entirely true. Fanning cools sweating animals because it accelerates the vaporization of the sweat. But if an animal does not sweat, and its skin is dry, fanning can not increase the vaporization rate, and therefore cannot cool the animal unless the environmental temperature is lower than the skin temperature. The (sweating) dairyman's assumption that because he is cooled by fans the (non-sweating) cow is likewise cooled is understandable, but not penetrating.

Fans are not even likely to increase the vaporization rate from the respiratory passages, because the moisture from these sources is already fanned by the respiratory movements.

It is true that even non-sweating animals give off moisture from the skin;[14] Jersey cows are said [15] to give off about 1 pound of moisture per hour by non-sweating methods. However, this non-sweating moisture, referred to as diffusion or osmotic moisture,[16] is probably independent of environmental temperature, and not a significant factor in the homeothermic temperature-regulating mechanism.

The foregoing discussion suggests the desirability of discovering some substitute for sweat glands which holds much moisture and permits good air circulation. We investigated in a preliminary way the influence of wet porous rubber sponge blankets on the respiration rate of sheep and cows, with results shown in Fig. 9. Wet blankets were put on sheep A and B at 10:30, while sheep C and D served as controls. In the blanketed animals, the respiration rate—which is the best index of a non-sweating animal's comfort with respect to temperature—immediately dropped from its initial level of about 190, to 160, 150, and finally 145. By 1 o'clock the blanket began to dry, and the respiration rate began to rise. When the blanket was removed, the respiration rate promptly attained its initial level.

5. Interrelation Between Sunlight, Temperature, and Feed Supply and Their Influence on the Seasonal Rhythms in Productivities and Efficiencies

The seasonal temperature rhythm is of course conditioned by the sunlight rhythm and, agriculturally, temperature is not separable from sun, season, and latitude.

Thus the rate of vitamin D production in milk is undoubtedly correlated with the light rather than with the temperature rhythm. The decline in production of normal sperm in rams during later summer is, on the contrary, due to the high environmental temperature [17] rather than to sunlight. The seasonal respiration-rate rhythm in cattle is due mostly to the temperature rhythm, although it is possible that sunlight and barometric pressure are also influential.

The reproductive rhythm appears to be conditioned by the sun rhythm in some species, by the temperature rhythm in others, and in still others by neither.[18] Thus deer, sheep, and goat come into sexual activity when the days become shorter; ferret, fox, field mouse, wild cat, hedgehog, and practically all the birds investigated (juncos, crows, canaries, starlings, turkeys, sparrows, doves, ducks, pheasants, quail, grouse) come into sexual activity only when the days become longer. Among plants, maize and soybeans bloom only when a certain limiting short day is reached; spinach, wheat, and rosemallow bloom only when a certain limiting long day is reached. On the other hand, some plants, such as buckwheat, and some animals, such as guinea pig, guinea fowl, and many domestic animals (cattle, domestic rabbit, house rats and mice) breed at all times of the year. There are other animals such as certain breeds of deer in Scotland, described by Marshall,[19] which do not begin to breed until "there has been a sharp frost," and "if there is an exceptionally mild autumn . . . . there is little mating, and very few calves will be dropped in the following year." Certain plants, including winter wheat and many northern wild flowers, must be kept at a temperature near or below freezing for some time to produce abundant growth and flowering.

Diet rather than temperature may be the limiting factor to the seasonal sex rhythm. Rapidly growing plants, such as are common in the spring, are said [20] to be very rich in gonadotropic hormones. The seasonal migration and breeding of some bird species may be conditioned by a combination of food and light rather than temperature factors. Birds require a long day for procuring food, which may cause them to migrate seasonally to the regions of longer days associated with greater food supply. This may be the genesis of the apparent photosensitivity of certain species.

We [21] have studied extensively the seasonal rhythms in metabolism, growth, and reproduction, one illustration of which is given in Fig. 10. We are not sure whether this rhythm is due to temperature, sunshine, food supply, or to a combination of the three.

In brief, the temperature factor is not separable from the light and food factors in conditioning various phases of productivity and efficiency on the farm.

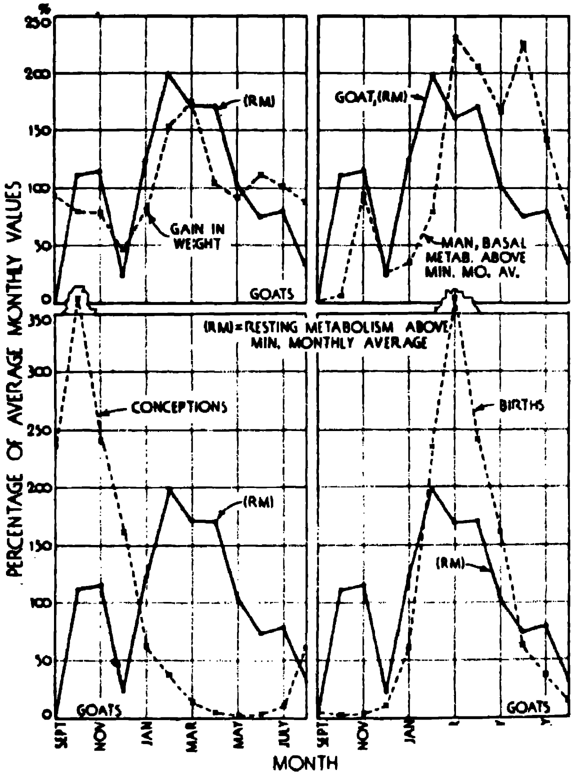


FIG. 10. Seasonal rhythms in growth, reproduction and heat production (R. M.) in the goat. Heat production rhythm in man. Note the similarity between the curves of man and goat.

Summary

According to their ability to withstand high environmental temperature, warm-blooded animals are divided into (1) sweating animals, exemplified by men, horses, mules, and asses, able to withstand great heat, particularly in dry moving air; (2) non-sweating animals, exemplified by cattle, sheep, swine, chickens, dogs, cats, rats, and rabbits; unable to withstand great heat.

When a sweating animal is placed in a hot environment it responds by sweating and sending its blood to the moist surface for cooling. This reduces the blood volume needed for carrying oxygen to the tissues. To compensate for this deficiency, the heart pumps faster, that is, the pulse rises. When a non-sweating animal is placed in a hot environment, it responds not by sweating, but by panting, that is, by rapid respiration rate. The skin is not cooled, because it is dry, and the blood is sent from the hot skin to the interior, with a resulting decrease in pulse rate. As the increased respiration rate in hot weather does not increase the vaporization rate to the same extent as sweating does, the non-sweating animal becomes overheated at relatively low temperatures (above 80 °F or 26 °C), with consequent increase in heat production (maintenance cost), decrease in productivities, and, of course, decrease in efficiencies of the productive process. We have presented practical suggestions for cooling non-sweating animals in hot environments by the use of wet, porous blankets.

Beginning with the "comfort zone," farm animals, especially of the non-sweating class, are very much less sensitive to declining than to rising temperature. Thus the productivities and efficiencies and comfort of farm animals are not reduced by decline in the environmental temperature from the comfort zone of 60 to 70 °F (15-21 °C) down to perhaps 0 °F, while, as previously noted, rising temperature above 80 °F overheats and seriously reduces the productivities of non-sweating farm animals.

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The Temperature Pattern of Laboratory Animals in Normal and Febrile States*

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The purpose of this paper is to present certain observations concerning the temperatures in various parts of the body of normal laboratory animals as influenced by various chemical and physical agents. Heat exchange through the skin and respiration, the influence of environment, and body metabolism have been studied at great length by numerous investigators. At the time when various physical agents were first being employed as means for producing febrile states in human beings for therapeutic purposes, no data were available which might give information upon which to establish the limits of normal and dangerous temperature levels within the body in such febrile states, nor were there data which would allow a correlation of the internal temperatures of the body during the febrile state.

Since it was found that the temperature of the many organs differs it is apparent that the situation is quite complicated—in fact it is so complicated that it is difficult to draw more than general conclusions from the data obtained in our experiments. It is for this reason that charts are shown to give a characteristic factual picture of what might be expected under certain conditions. Our data show that the temperature is extremely labile in any given situation in the body, and that surmises as to what might be the temperature under any one circumstance are often proved wrong on measurement.

In order to relate the temperatures of a number of organs to one another, a set of twelve copper-constantan thermocouples was used, ten of these being mounted in stock hypodermic needles and two in rectal applicators. The needles were from 7 to 10 cm long and of 16 to 19 gage (1.64-1.06 mm outside diameter). The 12 couples were arranged so as to be connected consecutively to a potentiometer by means of a 12-position selector switch. Each individual cold junction was imbedded in approximately 2 cc of Wood's metal surrounded by a glass envelope. The cold junctions were kept in a vigorously stirred water bath set at 37.0 °C. No oscillation of the measuring device could be detected which could be due to regulation of the cold junction water bath. The potentiometer was calibrated to 0.01 °C. Hot junction temperatures were calibrated in a water bath against a Bureau of Standards certified mercury thermometer supplemented by a Beckmann thermometer calibrated to 0.01 °C.

The thermocouples were usually placed in the deeper structures of the animal's body by guess, and their positions verified at autopsy. They were inserted to a minimum depth of 5 cm, with the exception of the eye (Fig. 5). The error introduced by conduction of heat along the steel thermocouple needle was assumed to be minimal and constant for any given location. Visual inspection through incision indicated that the amount of gross hemorrhage was very small, and at most extended only a short distance around the shaft of the needle even in an organ as vascular

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* Assisted by a grant in aid from the Rockefeller Foundation.

as the liver. While bleeding and clotting usually occurred within a restricted zone, apparently narrower than one millimeter around the needle, there was quite a zone of congestion followed by ischemia lasting from 15 minutes to one-half hour, with a return of what seemed to be a state of equilibrium and a "normal" blood flow through the area around the needle. Most of the experiments, particularly in the large animals, were carried out over a period lasting from five to eighteen hours.

Exactly "normal" conditions in laboratory animals cannot be achieved without great difficulty. It is possible to insert fragile needle thermocouples in the trained dog without anesthesia, but this is obviously impractical in most laboratory animals. The unanesthetized, quiescent, normal laboratory animal which is accustomed to being handled has a rectal temperature ranging between 36 and 37 °C, with a general average of 36.5 °C at room temperature over a range between 20 to 30 °C (mouse, rat, guinea pig, cat, dog, calf). It is unusual to find rectal temperatures as low as this because in the high-strung, although well-trained dog, for example, the activity due to frolicking before the experiment begins may cause the rectal temperature to rise as much as three degrees. Throughout the observation period, episodes which attract his attention and the dog's desire for notice produce activities which contribute to fluctuations in the temperature.

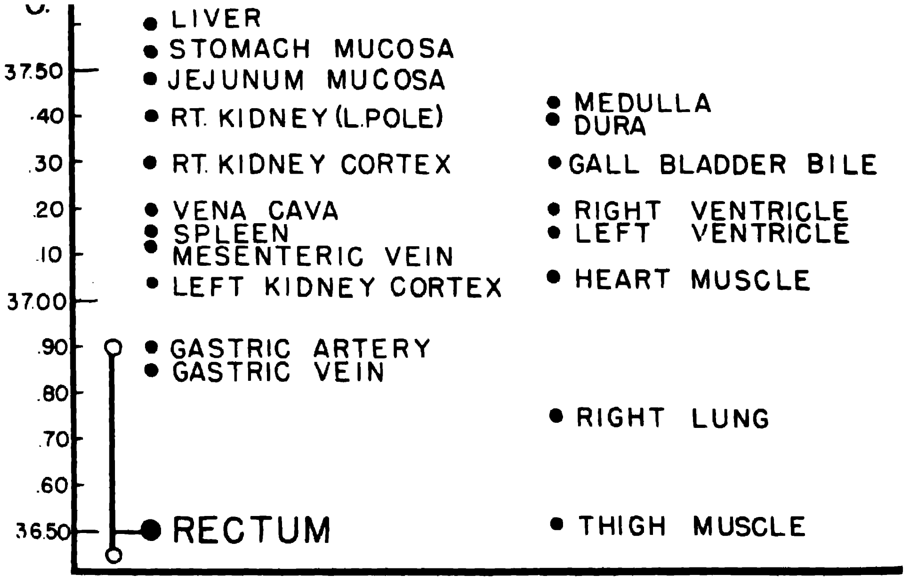

Fig. 1. Normal organ temperatures (gradients in calf).

On the other hand, anesthesia, while it eliminates conscious influences, sets up abnormalities: (1) by changing the general metabolism, and (2) by changing the circulation (apparently by dilatation of the subcutaneous vessels as well as others) which results in a rise in the subcutaneous temperatures and a fall in the general body temperature. In most cases a brief period of struggling while going under the anesthetic results in an increase of from 0.2 to 0.3 °C (rectal) in all laboratory animals. This rapidly falls to nearly the average rectal temperature, and then throughout the period of observation with a room temperature of 26 °C, the general body temperature slowly falls to reach, in cases of protracted observation under deep narcosis, levels as much as 2 to 3 °C below the usual rectal temperature for the animal. All the commonly used anesthetics seem to cause this gradual reduction of the rectal temperature. In prolonged, deep anesthesia (5-20 hours) the rectal temperature may fall to as low as 32 °C. Also the position of the animal, usually abdomen up, speeds the fall in the general body temperature because the direction of the hair is now reversed, and the less hairy areas of the body are exposed. This increased heat loss is also observed in the quiet, unanesthetized animal.

A study of the temperature levels in a large series of laboratory animals emphasizes the fact that a fairly wide range of temperatures is found among the various organs, and even within the various parts of the same organ. The range of temperatures within an organ (with the animal under anesthesia) may be as much as one-half degree centigrade, and the differences between the hottest and the coldest organs in the deep viscera may be a degree and a quarter. These differences, which are illustrated in Fig. 1 in the calf, may be the result of different metabolic rates in these organs. They are also a resultant of the heat gains and losses of each

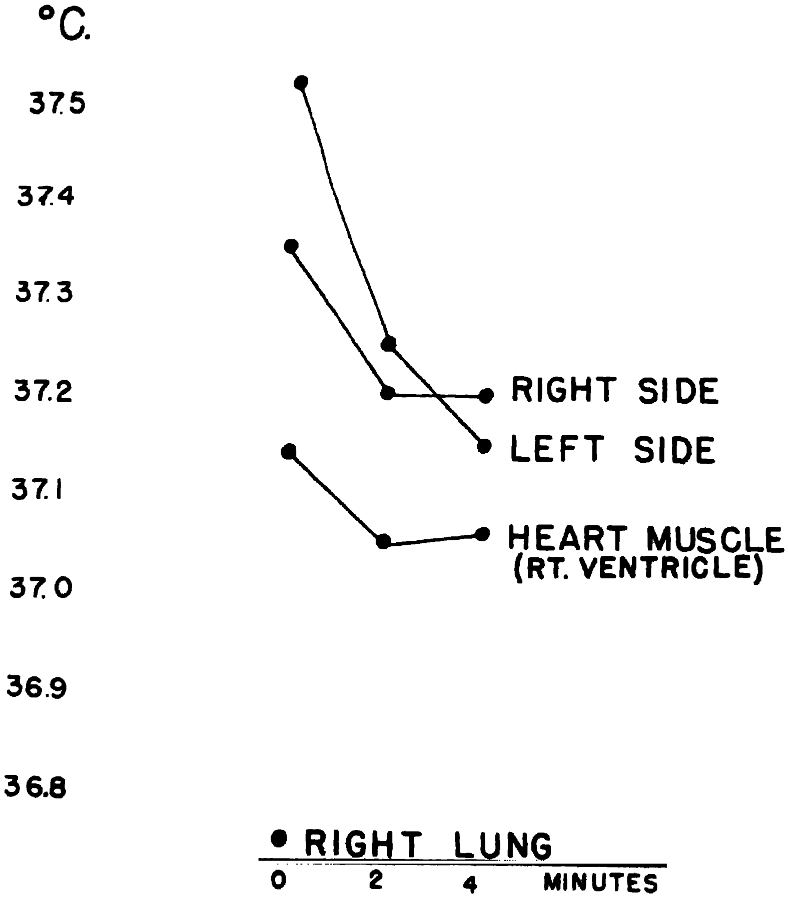

Fig. 2. Gradients in heart blood (calf).

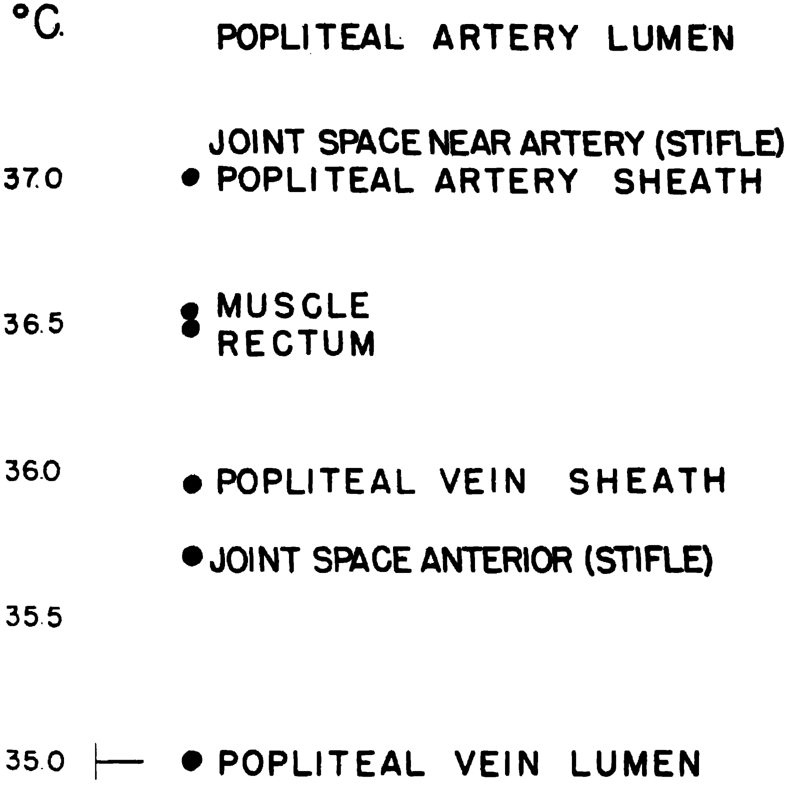

FIG. 3. Artery-vein gradients (calf).

individual organ. It will be noted in Fig. 1 that the rectal temperature of the calf fluctuated over 0.5 °C, averaging throughout most of the experiment around 36.5 °C. The higher reading represents the increase in body temperature which resulted from the muscular activity which occurred during the induction of anesthesia (chloral hydrate, intravenously). The other temperatures shown in Fig. 1 were recorded after "equilibrium" had been reached and were chosen as the most representative of the usual findings, although they are not to be considered as being constant temperatures by any means.

Fig. 2 shows a rapid fall in the temperature of the heart's blood (calf) with reversal of the temperature of the blood of the left and right sides of the heart. Although the total change involved in this instance represents only a few tenths of a degree, it serves to illustrate how difficult it may be to make any dogmatic statements about the temperature relationships of the viscera at any particular time.

In Fig. 3 are shown the various temperatures around the stifle-joint in the same calf under deep anesthesia, and after equilibrium has been established. This joint is as large as the knee joint in the adult human. The temperatures of the blood in the lumina of the popliteal artery and vein apparently influence greatly the temperature of the nearby portions of the joint space. The temperature of the joint near the capsule, which is very close to the popliteal artery sheath, has very nearly the same temperature as the latter, apparently by virtue of the heat transfer from the hot blood passing through this artery. The anterior margin of the joint space is 1.3 °C lower, probably because there is less blood flowing through this region; and it is less well insulated, being covered as it is only by a thin layer of skin, subcutaneous tissue, and joint capsule. There is a difference of 2.5 °C between the temperature of the arterial blood and that returning from the foot. There is no reason to believe that this low venous temperature is unusual, since values in this range or lower have been obtained in other experiments. The rectal temperature and the thigh-muscle temperature are almost identical.

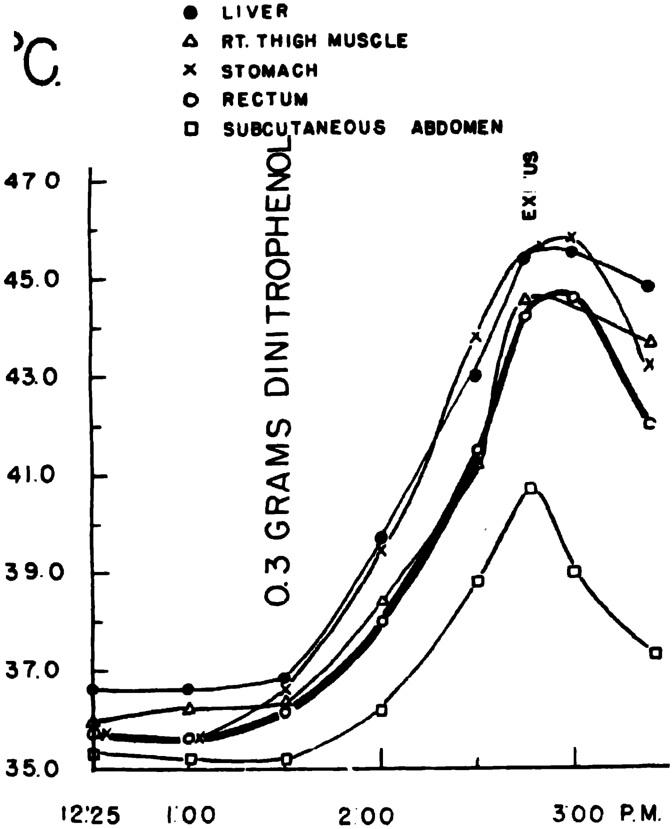

Fig. 4. Dinitrophenol (dog, 12.5 kg); amytal anestheesia.

It is of interest to study some of the drugs causing general elevations of temperature. Fig. 4 illustrates the effect of 0.3 of a gram of dinitrophenol injected subcutaneously in an animal anesthetized with amytal three hours previously. There is an immediate precipitous rise in all the body temperature levels (only five shown). The changes in the skin and superficial organs are apparently not as great because of heat losses to the outside, but in general the slopes of the curves of all of the viscera are roughly the same. It may be seen from Fig. 4 that when the deep temperatures have reached 45.3 to 45.5 °C, exitus occurs. Other observations on the same animal showed that the brain, spleen, and kidney also reached this level. The temperature of the lungs, superficially placed muscles, and other structures did not rise quite as high as this. Following exitus there was some overshooting, since the heating process continued for some time after vital functions had ceased. The subsequent cooling was like that which occurs after production of fever by other means. Smaller doses, such as 0.1 gram, cause elevation of the temperature to 43.0 °C, with subsidence gradually over a period of five or six hours to 39 or 40 °C. Summative effects may be obtained by the administration of another 100 milligrams. This is usually followed by exitus.

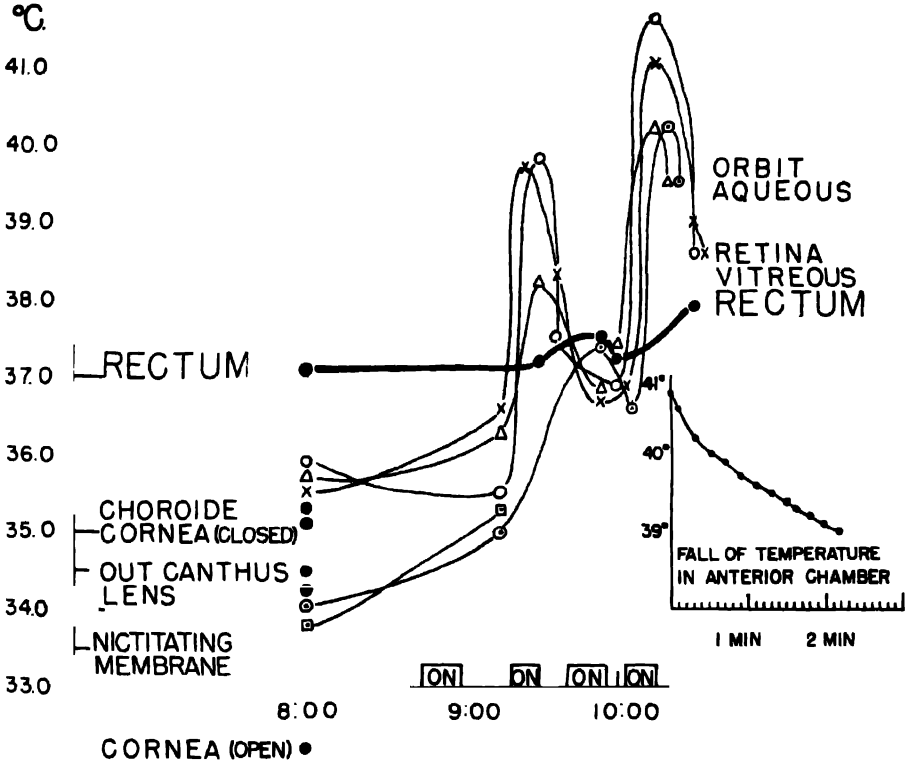

FIG. 5. Electrostatic field 28 meters; gradients in eye (dog); amytal anesthesia.

With the other methods of temperature elevation which are less rapid, exitus occurs when the rectal temperature reaches 43 to 43.5 °C with the brain and liver temperatures approximating 44 °C. With dinitrophenol the rectal temperature and body temperatures rise so rapidly that coagulation (solidification) of the tissues may occur at about the same time as exitus, with a rectal temperature of 44 ° C and deep-organ temperatures approximating 45 to 45.5 °C. The rapidity of rise of the temperature therefore bears an important relationship to the temperature at the time of exitus.

Fig. 5 shows the effectiveness of "28 meter waves" in influencing the temperature of the eye. The condenser plates were put across the antero-posterior diameter of the head, and the radiation broadcast to the head. The character of the radiation was such that no temperature-measuring device could be used successfully in the electrostatic field, and it was necessary to remove and replace the thermocouples after the heating period. This replacement can be done under direct visualization in the eye with some success. The experiments show that it is possible to heat the eyeball by means of short radio waves. The circulation and other mechanisms for heat loss are very effective, however, in reducing the temperature as soon as the current is turned off. Thus the curve does not represent the maximum temperature obtained, but illustrates the highest observed after the delay involved by the reinsertion of the thermocouple. It was noticed that the cornea had a temperature of 32.2 °C with the eye open and 35.1 °C with the eye closed. The cornea apparently is the coldest part of the body, probably because of the large amount of evaporation which occurs from its surface. The small graph inside Fig. 5 shows the very rapid fall of the temperature which occurs in the anterior chamber of the eye. Because of the difficulty of making temperature measurements, extensive experimentation with short radio waves was abandoned. Enough was done, however, to indicate that, aside from the method of application, the temperature elevation in the body

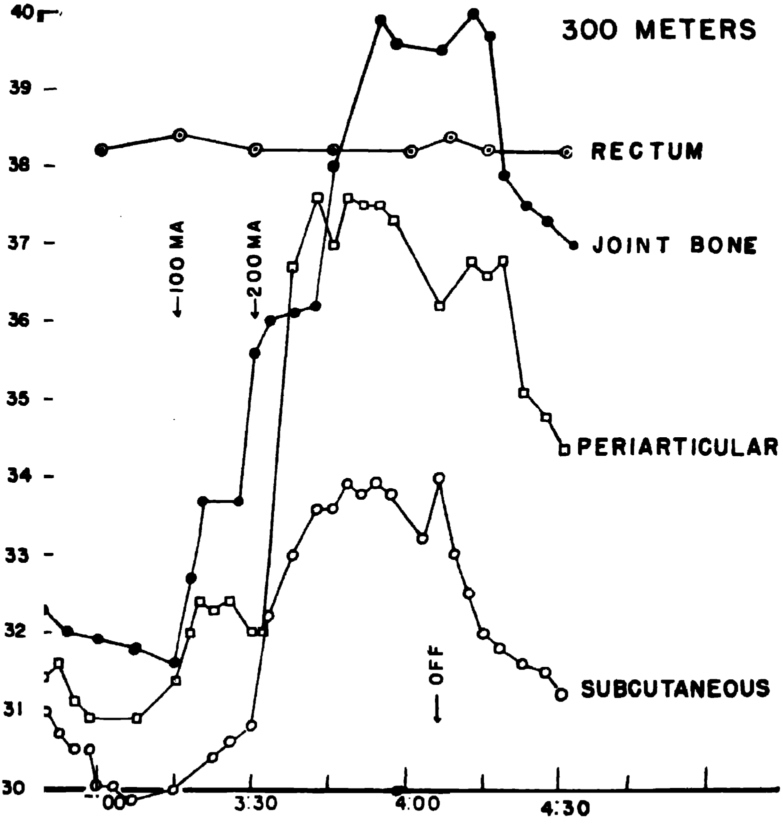

Fig. 6. Cuff electrodes.

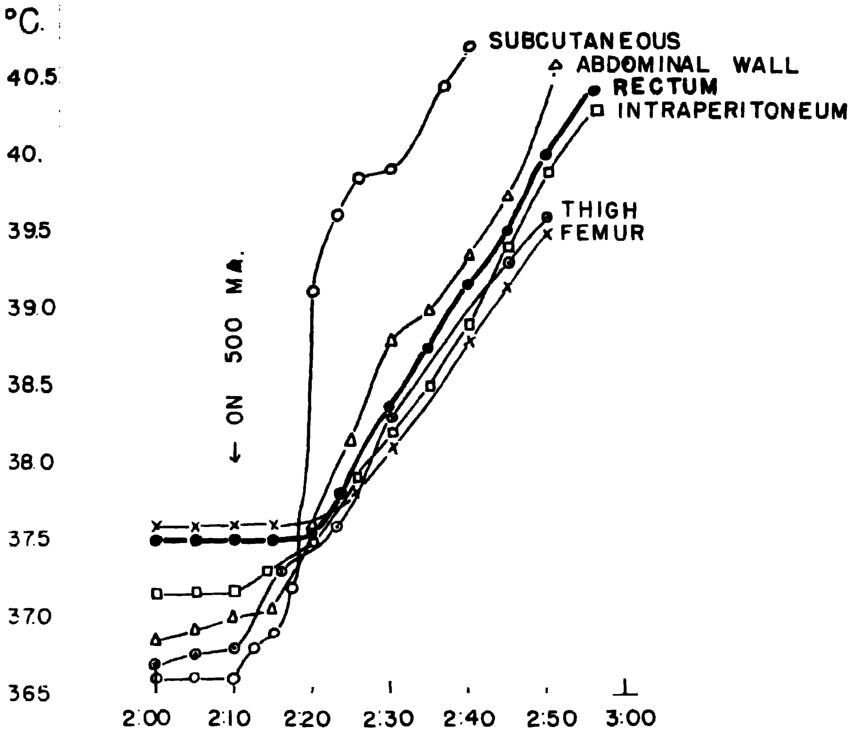

Fig. 7. 300 meters contact electrodes; 200 sq cm abdomen to back (25-kg dog) : amytal anesthesia.

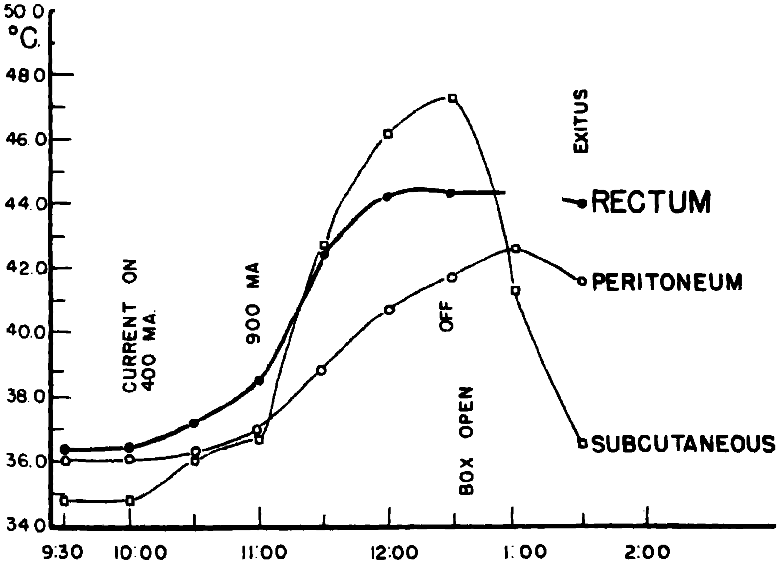

Fig. 8. 300 meters contact electrodes; 200 sq cm abdomen to back (28-kg. dog); amytal anesthesia.

produced by the absorption of this energy was little if any different from that observed with diathermy currents. It is impossible to say at the present time whether practical concentrations of heat can be obtained beneath the body surface by selective heating by different frequencies.

Fig. 6 shows the result produced by diathermy in the carpal joint of the calf. The currents are conducted between cuff-contact electrodes, and the anatomical configuration is such that the currents, after penetration, may readily follow fascial planes and bone and joint structure in what amounts to electrically parallel circuits. Under such conditions the bone is apparently a better conductor, so that the current may be quite heavy through the joint which is midway between the electrodes. The illustration is probably comparable to what may be obtained in the therapeutic use of diathermy when carefully and properly done, although it is apparent that the time consumed in raising the joint temperature 8 °C above its original temperature was considerably over one hour, and even then the elevation above rectal temperature was less than two degrees.

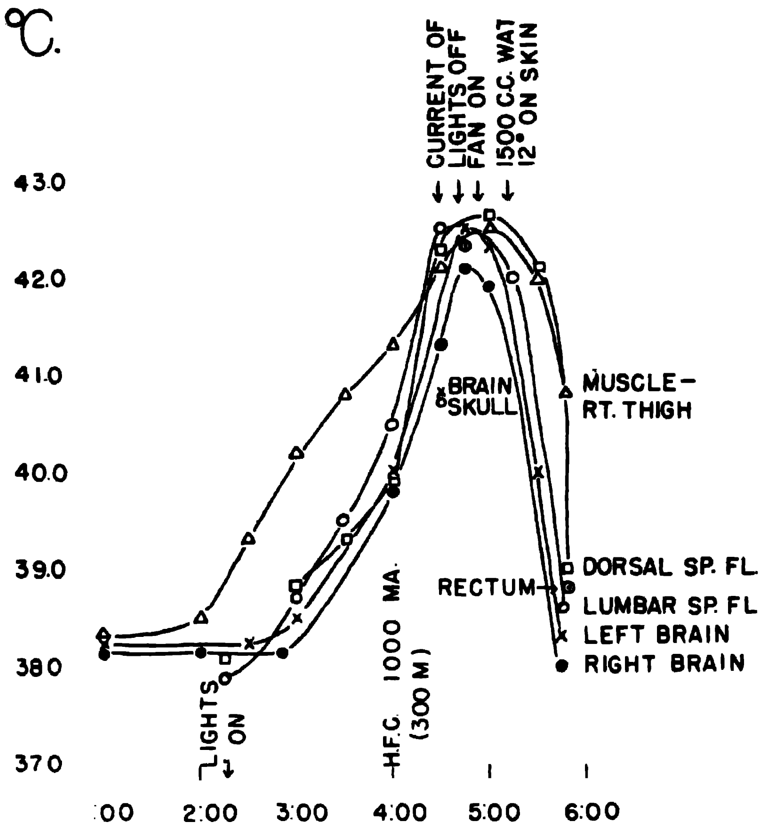

FIG. 9. Temperature gradients, C.N.S. (dog).

Fig. 7 illustrates what is more nearly like a series electrical circuit. The contact electrodes are placed on the abdomen and back. The current must pass across muscle and fascial planes, and under such conditions the subcutaneous, abdominal wall, and intraperitoneal temperatures reverse their usual relationship. In this case the thigh and femur temperatures roughly parallel the slope of the rectal temperature even though they are out of the electrical field, because of the general distribution of the absorbed energy by the circulation. Larger electrodes on the trunk allow the passage of greater currents, so that the whole body temperature may be elevated to any desired level within a reasonable length of time.

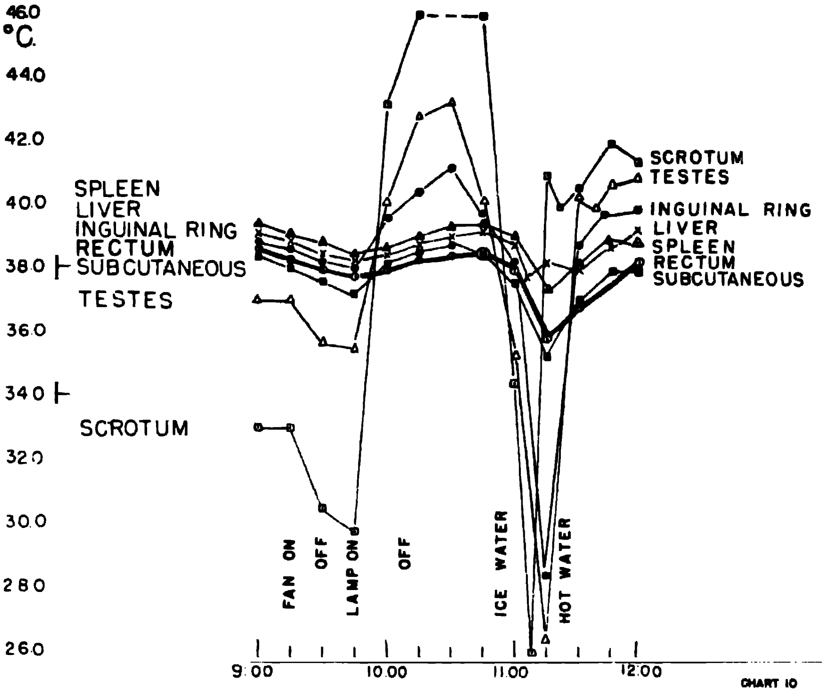

FIG. 10. Temperature gradients (rabbit).

Fig. 8 demonstrates that it is possible to raise the temperatures to rather high levels and maintain them for a long time before exitus occurs. In this experiment the current was increased enough to raise the subcutaneous temperature to the point of coagulation (above 46 °C). The rectal temperature rose to 44.1 °C where it was maintained for 30 minutes. The animal was obviously *in extremis* for all of this time, yet exitus did not occur until one hour and a half after the temperature had reached 44 °C. Peritoneal temperatures outside of the electrical field did not rise as rapidly nor as high as did the rectal temperature, although the other deep-organ temperatures were from 0.2 to 0.5 °C above the rectal temperature. This low peritoneal temperature may be explained by the position of the thermocouple, which was just below the anterior abdominal wall and surrounded by intestinal loops which insulated it from the near-by organs and the large blood vessels. The rapid cooling of the subcutaneous tissue as soon as the treatment cabinet is open is well shown.

Fig. 9 illustrates the summative effects of infrared and high-frequency radiations, and illustrates in addition the changes occurring in the central nervous system. The rectal temperature is not shown, but it followed that of the brain, except

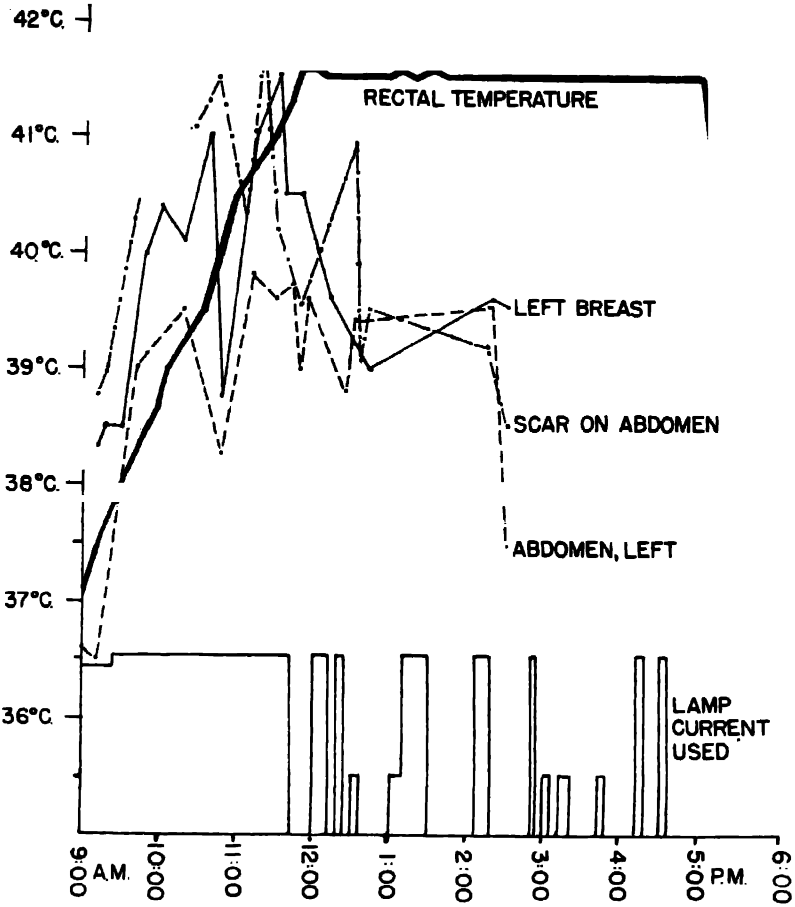

FIG. 11. Skin temperature gradients during artificial fever (man) ; no narcosis.

for the last observation at the termination of the experiment where it lay between the dorsal and lumbar spinal fluid temperature. The rate of fall in the brain is considerably more rapid than that in rectal temperature. The agreement in the temperature fluctuations of the brain and spinal fluid is striking. The effect of the rapid cooling of the body when cold water is applied to the anterior skin surface of the trunk is demonstrated.

Fig. 10 illustrates the reversal of gradients which can be obtained by the application of infrared radiation to the trunk and body of the unanesthetized rabbit, and the restoration of the pattern of the gradient by withdrawal of heat with the application of ice-water. The extremes in the superficial temperatures, particularly that of the skin of the scrotum, extend over a range of 20 °C. The first 15 minutes of observation represent the fall in deep-body temperatures, which results when the rabbit is placed belly up so that the hair no longer insulates properly. The immediate change amounts to from 0.1 to 0.2 °C, and in other experiments with a smaller decrement as time goes on, the animal's body temperature gradually reaching an equilibrium point, which is considerably influenced by the room temperature.

The cooling effect of a fan and the effect of thermal lag and overshooting are illustrated.

Fig. 11 shows the change in temperature of the skin in three places on the trunk of a female patient receiving artificial fever therapy in the radiant energy cabinet. The air in the cabinet is not stirred and the radiation source is a row of lamps above the patient. The fall from the peaks of the skin temperature represents a sudden out-pouring of sweat. It is evident that this sweating is not constant in any given area nor does the patient sweat equally over the body. The evaporation of water from the surface of the skin diminishes as the jacket of air immediately around the patient approaches saturation. As can be seen from the amount of power used, the largest energy input was required during the rise of the temperature, and less and less was required for maintenance. During the last two-thirds of the treatment, the skin temperatures were 2 to 4 °C or more below the rectal temperature, and during this period the cabinet temperature may be very close to that of the room. The reduction of the temperature is achieved by opening the

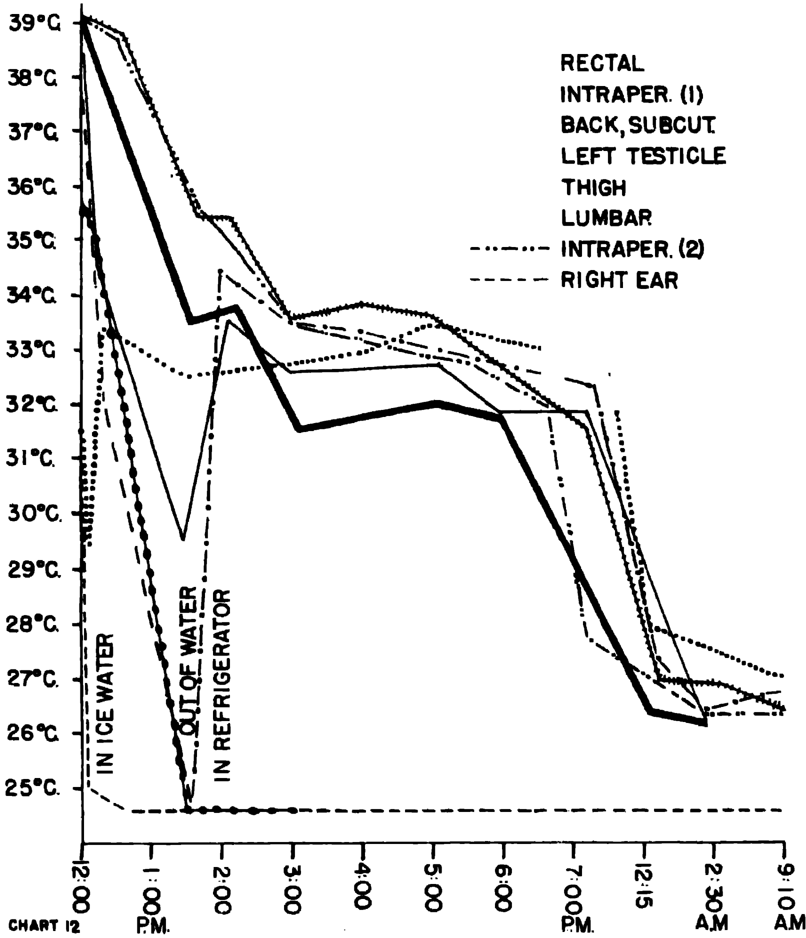

Fig. 12. Temperature gradients in freezing experiments (ice pack and partial immersion in water) (rabbit).

cabinet, thus eliminating insulation, and by blowing colder room air across the skin with a fan. This stimulus in a well hydrated patient often calls forth a profuse perspiration, the evaporation of which materially enhances the fall of the body temperature.

Fig. 12 (with Dr. Irving Ariel) shows the beginning of a prolonged immersion of the rabbit in ice-water by way of comparison with temperature gradients in the heated animal. The subcutaneous, testicular, and intraperitoneal temperatures fall precipitously. The ears become pale and their temperature falls as fast as that of the testicle even though the upper ⅓ of the rabbit is exposed to room air which is approximately 20 °C. The rectal temperature falls at a much slower rate. The intraperitoneal temperature, due to slight shifts in the position of the thermocouple resulting from movement of the animal, varies erratically, indicating that the temperatures of near-by structures are not uniform. On transfer of the animal from the water to the hypopyrexia cabinet the testicle temperature rises and the rectal temperature remains in general the lowest of the deep-body temperatures recorded. The temperature of the ears remained below our temperature scale until the general body temperature of the animal returned to nearly normal. There are greater extremes of temperature in the various parts of the body at these low temperatures than there is in the case of elevated temperatures.

In general, the body of the animal seems better adapted to withstand a fall of 10 °C (rectal) than it is to stand a rise of 6 °C (from 36 to 42 °C rectal). The shrinkage of tissues and the increase in viscosity of the blood, etc. in the cold state apparently are better tolerated than the dehydration and other phenomena resulting from the attempts of the body to cool itself while in the heated state. Continued elevation above 41.7 °C in animals and man is fraught with hazard, and in the rabbit temperatures below 26 °C are dangerous, although a number of our rabbits have survived 10 hours at 11 °C (rectal temperature).

Conclusions

(1) There is no constant and fixed normal temperature within the body. The rectal temperature fluctuates under "normal" conditions near 36.5 °C ± 0.5 °C in all the common laboratory animals. Deep viscera, including the brain, have temperatures which are higher than this by 0.2 to 1.2 °C, and superficial structures are considerably lower. The temperatures of the viscera probably depend a good deal upon their intrinsic metabolic activity at the moment for their position in the temperature scale. Thus psychic influences, air temperatures, and many other factors will influence observations made on normal animals.

(2) Anesthetics cause disturbances in the superficial temperatures and result in a general reduction of the whole body temperature.

(3) In febrile states, the usual temperature relationships may be modified or even reversed, depending somewhat upon the method used to create and maintain the elevated temperatures. The results of the use of specific chemical and physical agents are discussed and depicted in the temperature curves. The more localized application of energy results in steeper gradients within the area of absorption modified by the blood flow and other internal as well as external factors. This same conclusion may be drawn from the experiments dealing with the local withdrawal of heat.

Acknowledgments

We would like to acknowledge the assistance of Dr. Charles Carpenter and Dr. Ruth Boak in compiling the data represented in Figs. 1, 2, and 3. We also wish to acknowledge the work done by Dr. Irving Ariel in connection with the data of Fig. 12.

Chapter 6

Temperature and Its Regulation in Man

Temperature Sense in Man

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The sensory mechanisms of the skin function to inform the individual of his environment and enable him to avoid unfavorable conditions. Nerve fibers are sensitive to many kinds of stimulation, among them injuries of almost any type. The receptors for pain are probably undifferentiated fine nerve fibrils spread widely through the skin and deeper tissues and capable of being stimulated by extremes of heat and cold as well as by other injuries. Hardy, Wolff and Goodell[1] have recently measured the threshold thermal changes for the production of pain by heat, which they find to have a value of 0.218 cal/cm^2/sec for 3 seconds. This must be contrasted with a threshold for warmth of 0.00015 cal/cm^2/sec, a value only 1/1900 of the former. The function of specialized receptors for temperature is therefore the reduction of the threshold value for stimulation, so that temperature changes, which fall far short of producing local injury, may yet be evaluated. They represent a special evolution of the simpler and more primitive mechanism—one adapted not only to prevent injury but also to assist in temperature regulation.

Pain from Temperature Changes

The more primitive mechanism of pain sensation may react to both heat and cold. For neither heat nor cold is the threshold dependent on the actual temperature of the stimulus, but rather on the relation of this temperature to that of the skin. When the skin temperature is low, mildly warm stimuli below the normal body temperature of 37° may be painful (Yoshida,[2] earlier still Fujita, and more recently Hardy et al.[1]) The threshold for the production of pain by heat is not altered by the area exposed.[1] Pain produced by cold has been studied less quantitatively.[3]

Thermal Receptors

The special receptors for cold and warmth have received provisional, though not absolute, identification. A hot sensation is probably a compound one with elements of warmth, so-called paradoxical cold (cold receptors stimulated by considerable warmth), and pain. The receptors for cold appear to be Krause's end-bulbs, small encapsulated bulbs of nervous tissue about 40 μ in diameter found close to the surface, just superficial to, or in the outermost layers of, the blood vessels. The evidence is mainly dependent on observations by Strughold and Karbe.[4] A spot sensitive to cold could be identified on the conjunctiva of Strughold's eye; methylene blue washed over the surface penetrated and stained a Krause end-bulb in this position. The staining was associated with loss in sensitivity to cold. Later the staining disappeared and after a few days sensitivity returned. The receptors responsible for warmth appear to be somewhat larger masses of nervous tissue, known as Ruffini's end-organs. These lie deeper in the skin or subcutaneous tissue. at depths where blood vessels are both numerous and arranged in complicated patterns of arterial and venous networks. The exact relation of the receptors to these vessels is not known. The evidence for their involvement in sensations of warmth is dependent mainly on work by Williams, McGlone and myself.[5] As it has been criticized, I wish to take time to defend it.

There is a definite latency between the time a stimulus is applied and that at which the subject signals sensation. This delay or "reaction time" is of the order of 0.3″ to 0.5″ for cold and 0.5″ to 0.9″ for warmth. Theoretically, part of this latency should depend on the time taken to develop the threshold change in temperature, and should vary with the distance of the receptor from the stimulus and the strength of the stimulus. We attempted to estimate the depth of the receptors by determining the latency when the distance between the stimulus and receptor was varied. The experiments received some notoriety as the "fish-hook-prepuce" experiments, since we utilized a double fold of prepuce suspended by weights attached to it by fish-hooks. The thin double fold of 1 to 1.5 mm thickness could be stimulated from either side. If a spot sensitive to warmth was present on only one side, sensations of warmth could still be produced from the more distant side of the fold, but they developed with a latency which usually considerably exceeded (0.5″ or more) that observed with stimulation of the other side. The rate of thermal transmission was measured by thermocouples of very light wire attached to both surfaces.

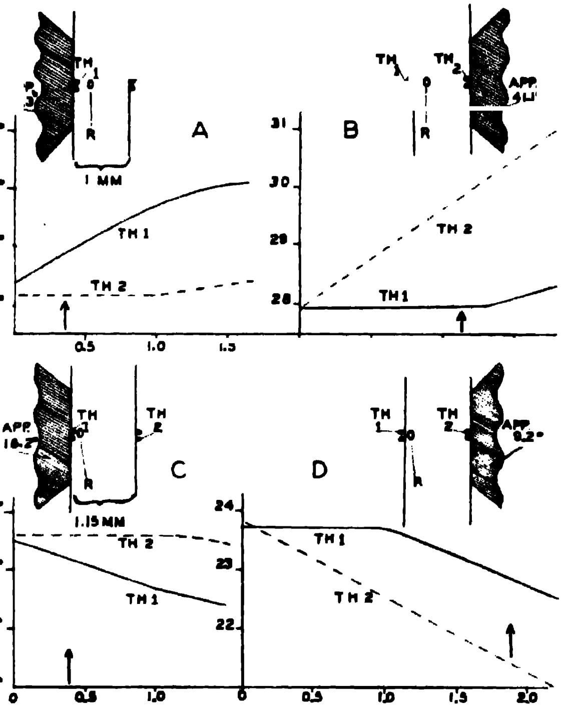

FIG. 1. The conditions of stimulation of a prepuce fold with warmth are indicated in *A* and *B*. Th 1 and Th 2 represent the thermocouples on the two surfaces, *R* the assumed position of the receptor, and App. the applicator with the temperature of the circulating water indicated. The initial and later temperatures of the surfaces recorded by the two thermocouples are shown below. The arrows indicate the latest probable times for the generation of the sensation (0.14 sec before the signal was made). *C* and *D* represent similarly an experiment with cold. Times are shown on the abscissae in seconds, temperature changes in °C as ordinates.

This rate of transmission was of the order of 1 mm/sec. Equations of the following type could be utilized to calculate the depth of the receptor

$$t_1 = \frac{d}{v} + y \text{ and } t_2 = \frac{D - d}{v} + y$$

where t_1 and t_2 are the two observed reaction times, d is the depth of the receptor, D the thickness of the fold, v the rate of thermal transmission, and y the time lost in other processes.

A semidiagrammatic representation of such experiments is shown in Fig. 1 (which represents the conditions obtaining in Experiment 5, stimuli 11 and 5, and in Experiment 1, stimuli 6 and 16 of the original report). The relative positions of the thermocouples and the thermal applicator, as well as the assumed position of the receptors, are shown above and the temperatures actually recorded on the two thermocouples below. The heavy arrows indicate times 0.14 second earlier than the times when sensations of warmth (A and B) and cold (C and D) were signalled. These arrows indicate, therefore, the latest times these sensations could have been generated, for the actual nervous processes involved in the response probably lasted at least 0.14 second. It is clear that in both experiments the sensitive receptors were much closer to thermocouple 1 than to 2. By the equation given the depth calculated for the receptor for warmth (from the data of A and B alone) is 0.24 mm and the time taken in developing the threshold change in temperature together with that of the nervous reaction is 0.26 second. It will be noted that in the case of cold the sensation is so delayed with reverse stimulation that no such equation can be applied.

Using this crude approximation, the receptors sensitive to warmth were calculated as having depths of either 0.3 or 0.6 mm, the latter value representing the center of the fold. Calculations leading approximately to the same depths could also be made by assuming that the differences in reaction times to touch stimuli and to strong warm stimuli were mainly dependent on the time taken for thermal transmission. The number of warm spots was found to be about 1/cm.^{2} An independent histological study of the receptors of the prepuce made by Dr. R. G. Williams gave a depth of 0.3 mm for Ruffini's end-organs with a distribution of about 1/cm.^{2} No such organs were found at 0.6 mm. However, in preparing the specimens, subcutaneous connective tissue had been removed, and consequently new preparations were made with preservation of this tissue. The Ruffini end-organs predicted on physiological grounds were found, again to the number of about 1/cm.^{2}

Similar calculations for the depth of the cold-spot receptors could be made only by the second method (comparison with tactile reception); the equations with two unknowns gave absurd values (depth commonly negative) for reasons to be discussed later. The second method indicated a depth less than 0.17 mm and probably less than 0.11 mm. The number of identifiable spots was 6 to 12/cm.^{2} The independent histological study of Krause's end-bulbs made by Williams showed a population for the prepuce of about 15/cm^2 at a depth of 0.1 mm. The agreement was therefore good.

The conclusions reached have been criticized by Jenkins,[6] who argued that the latency of sensations should also be varied by the strength of the stimulus. Not finding such variations, he discarded our conclusions. His criticisms are not valid. Thermal transmission in the skin is a process complicated by large capacity effects, and movement of heat along irregular channels by moving columns of blood. The system is so complicated that the conditions are not accurately covered by the ordinary equations for thermal transmission. For instance, in working with a fold of prepuce it is not uncommon for the temperature change recorded by a thermocouple 1 mm distant on the opposite side of the fold to exceed that on the surface actually touched. Such anomalies usually depend on the presence of a large venous channel circulating blood immediately beneath the couple showing the smaller change. Table 1 gives some of the data arranged to demonstrate that in our experiments there was no evidence that the rate of thermal transmission was measurably changed by the strength of the stimulus. Though with more intense stimuli the threshold change in temperature required to stimulate the receptor should be attained more rapidly, the reaction time might not be much altered, if this time represented a small proportion of the total time consumed. Actually other factors play important roles and there is no relationship between the strength of stimulus and the reaction time for sensation, except for cold stimuli, which only slightly exceed the threshold (Table 1). In the latter case the delay is probably within the central nervous system. The absence of variations in latency described by Jenkins was predictable on our data.

Table 1. Rate of Thermal Transmission and Strength of Stimulus.

			Rate of thermal transmission		Reaction times of sensation (sec)	
Exp.	Stimulus mean temp. diff. (°C)	No. of observations	To start of change (mm/sec)	To max. rate of change (mm/sec)	Normal stimulus	Reversed stimulus
6 Warm	4.2	4	1.31	0.83	0.53	1.49
Fold 1.9 mm	10.1	6	1.15	0.73	1.10	(2.31)
	13.5	4	1.28	0.74	1.14	5.27
	16.7	3	1.50	0.76	0.72	1.56
1 Cold						
Fold 1.15 mm	3.2	3	0.90	0.58	1.35	6.05
	5.3	2	0.94	0.50	0.62	...
	6.7	5	1.31	0.58	0.95	3.00
	12.8	3	1.31	0.56	0.61	2.22

The thermal changes start on the near surface at their maximal rate; on the far surface they start slowly and only reach a maximal rate of change later.

The question of the identity of the receptors is not of mere academic interest. If identity is established, it should be possible not only to investigate the relationship of these receptors to the blood vessels but also to utilize these relationships to understand the mechanisms concerned. For the moment the receptors for cold appear to lie on the edge of the vascularized area, those for warmth between layers of vascular networks. If the former could serve to measure the thermal gradients between the circulating blood-stream and the tissues, and the latter the gradients existing between in-going arterial and out-going venous bloods, the mechanisms would be admirably adapted for measuring the effectiveness of skin radiation. For the present such ideas have no adequate experimental background.

Nerve Impulses from Receptors

The receptors concerned, when stimulated, undoubtedly induce a series of impulses up the nerves connected with them. These impulses must resemble those from other receptors. The sensations are identified as thermal, since they have anatomical relationships in the periphery with thermal receptors, and in the central nervous system with tracts concerned with thermal sensation. As with other sensory and motor nervous mechanisms, the intensity of the effect depends on the number of nerve fibers affected and on the frequency of the impulses passing up any single fiber. The amplitude of any single impulse remains unchanged. The effect on frequency of discharge may be demonstrated in single nerve fibers coming from receptors sensitive to temperature found in the ray fish Raja, described by Sand.[7] Some of his data are shown semidiagrammatically in Fig. 2. These receptors maintain a constant stream of impulses at a frequency which is greater the higher the temperature (see Fig. 2 for the first 4 seconds). However, a fall of temperature causes a temporary increase, not a decrease, in the frequency. The consequent complex changes produced by a sudden change in the temperature level are well demonstrated in the figure. Whether the human receptors maintain an incessant but variable rate of firing, or whether they fire only when stimulated, is uncertain. In either case the changes with stimulation are likely to be at least as complicated as those shown.

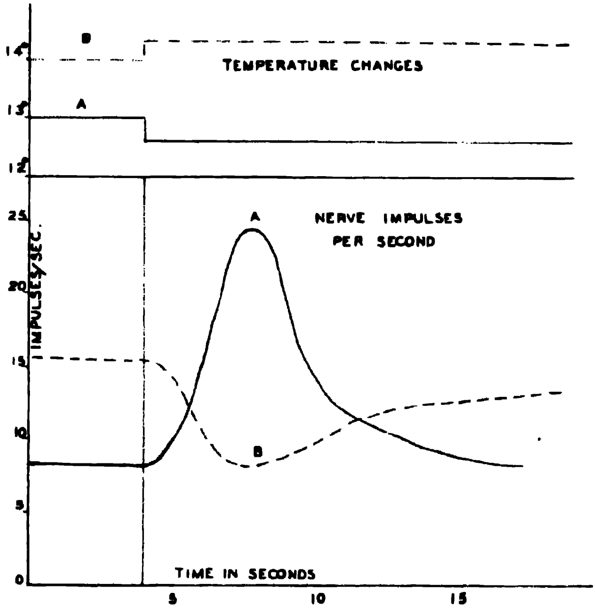

FIG. 2. The frequencies of the impulses passing up a single nerve fiber in the ray are shown as ordinates in relation to time in seconds as abscissae when the temperature of the fluid bathing the receptor is altered. The degree of alteration in temperature and the time of its occurrence is indicated above. (Data from Sand.)

Spatial Summation

Impulses transmitted by the nerves to the central nervous system produce, no doubt, central effects but may give rise to no conscious sensation. Only if these impulses are sufficiently numerous do they excite nerve cells, which then carry impressions to centers of consciousness. The impulses may increase in number to the extent necessary, either because the stimulus is great enough to cause a more rapid rate of firing from a single receptor, or because the stimulus affects a number of different receptors. The impulses act as though they converged on some group of cells, where the impulses from different receptors could summate. The effect is that both the threshold stimulus for sensation and also conscious impressions of the intensity of sensation are functions of the area stimulated. Whereas the effects of painful stimulation summate only on a quantity basis, those of temperature summate on both quantity and intensity. Stimulation of a large area is recognized as such with stimulation both by pain and temperature. Only with thermal stimulation is the subjective estimate of intensity modified not only by the strength of the stimulus, but also by the area to which it is applied. The former may be compared with electric batteries connected in parallel, the latter with similar batteries connected partly in parallel and partly in series.

The probable existence of this "spatial summation," as it is called, has long been recognized, but the recent work of Hardy and Oppel,[8,9] supplies the first real quantitative study in this field. The work they have done demonstrates that receptors for cold are stimulated by a fall in temperature of 0.004 °C/sec and those for warmth by a rise of 0.001 °C/sec, if such rates of change are maintained for 3 seconds. Yet any such change in a single receptor falls far short of producing any conscious sensation. Only when impulses from a large area can be fused does conscious sensation result from such weak stimulation. They have determined the necessary threshold stimulus for sensation in terms of the area affected. Where the sensitivity of the skin per cm^2 is uniform, as it is for warmth on the forehead, the data on threshold stimuli may be stated in the form

$$\text{Log } I + 0.78 \log A = 2.09$$

where I is intensity of radiation and A is the area irradiated.[8] With cold the capacity for spatial summation is somewhat less than that for warmth, though the receptors are more numerous.

Technical Difficulties

I would like to digress for a moment in regard to the methods of measurement employed. Hardy and Oppel have used as stimuli not only radiant heat but also a reflection device to intensify radiation from the skin and so to get, as it were, radiant cold. The stimuli are ideal in that they interfere in no other way with the normal condition of the skin, though they are limited in that they cannot be applied to a single sensitive spot. The same workers have measured skin temperature by utilizing its radiation. These methods are capable of great refinement and accuracy. For our own work light manganin-constantan thermocouples of wire of 60 to 80 μ diameter were utilized, and were strapped to the skin lightly at each end to prevent interference with the circulation. Stimuli were applied by using metal applicators in which water circulated, and studies were made mainly on single sensitive spots. In spite of the use of such different methods as well as of different parts of the body it is interesting that the threshold values we obtained for stimulation of single receptors fit the extrapolated curves of Hardy and Oppel. In the few observations we made on stimulation of large areas to determine the threshold values for sensations of warmth and cold, the crude method we used (slow cooling or warming of a large stirred water bath) did not allow precise measurements. The thresholds we obtained were consequently only roughly stated, namely for warmth 0.0017 to 0.005°/sec and for cold 0.0025 to 0.004°, but considering the crudity of the method they agree well with those of Hardy and Oppel of 0.001°/sec for warmth and 0.004 °C for cold. Gertz[9] in 1921 reported thresholds in baths as low as 0.004° for warmth and 0.0025° for cold. Probably the ratios of the thresholds of warmth and cold to each other are not the same at different skin temperature levels.

An illustration of the difficulty of exact standardization may be seen in the records of the changes in surface temperature when a metal applicator is placed on the skin. The surface temperature does not rapidly assume that of the applicator, as it theoretically should. This discrepancy depends on one's definition of surface.

The thermocouple wires, however fine, are by no means infinitesimal in relation to the depths concerned. The metal plate imbeds them in a groove in the skin, so that they have an effective depth of something less than 0.1 mm relative to the surrounding skin and are only slightly in contact with the applicator (see Fig. 1). The real surface temperature in relation to the receptor cannot be precisely stated; it may be that of the groove or that of the surrounding surface.

Technically it is also doubtful how far any thermal stimulus can be limited to any single receptor or group of receptors. One may assume that the initial response, if rapid, is due to those receptors in the immediate neighborhood, but one cannot be sure that additional receptors do not exist at a greater depth, since at such depths they could not be recognized as sensitive "spots." In the case of warmth, such deeper receptors probably exist, for receptors in the subcutaneous tissue, which are recognizable as "spots" beneath the thin skin of the prepuce, would probably not be so recognized where the skin was thick. Sensations of even deeper origin may exist for Ruffini's end-organs have been described in the periosteal coverings of bones. Whether there are also deep sensations of cold is still more uncertain, but not improbable. Krause's end-bulbs have been described in the synovial membranes of joints, and numerous encapsulated end-organs of somewhat similar structure are found in many deep tissues. Though sensations of cold are often ascribed to deep tissues, there is no unequivocal evidence of sensations of cold of deep origin.

Statistical evidence has been advanced to show that the grade of sensation is not related to the number of identifiable cold or warm spots of the area. In view of the numerous uncertainties, such discrepancies do not disprove the essential importance of these spots in generating the sensations. The whole story is not yet known.

Mode of Stimulation

The mode of stimulation remains merely a subject for speculation, though some facts are known. So far the subject has been discussed as though the stimulus was the rate of change in temperature. This is however improbable. As Gertz[10] showed in 1921, a hand maintained in water at 24° for about ½ hour loses the sensation of cold. If water at 12 to 15°, is used the sensation of cold persists, though it becomes weaker and is often ascribed subjectively to the deeper tissues. The sensation of cold undergoes periodic fluctuations, as does also the rate of blood flow. In one such experiment sensations persisted when there was no change in the superficial temperature measurable even in 20 minutes[11] by thermocouples imbedded in the tissues at 0.8 and 2.3 mm depth, and when the only abnormalities were somewhat steepened thermal gradients.

The possibility of persistent sensations without change in temperature is still more evident with warmth. Immersion of the hand in water at 40 to 41° maintains sensations of warmth even after 1½ hours' immersion; a steady state must certainly be acquired long before this time. Yet a hand in a bath at 41° may temporarily give no sensation of heat if it has been previously immersed for a long time in water at 42°. The obvious explanation is that sensation depends on a spatial thermal gradient and not on a rate of change. The blood with a temperature of 37 to 38° flowing rapidly through an arm immersed in water at 41° must maintain permanently a steep thermal gradient near the surface of the limb. If the surface temperature is suddenly increased, the sensations may be much exaggerated and the sensations may then be correlated with the rate of change of temperature. This is understandable, for rapid alterations in temperature are associated temporarily with much steeper gradients. Similarly when an arm is moved from water at 42 to 41°, the transition will tend to obliterate the superficial gradients during the period of readjustment, and the temporary loss of sensation of warmth is to be expected on a gradient hypothesis.

Even thermal gradients do not account for all thermal sensations. Ebbecke[12] analyzed the sensations of temperature which result when the blood flow to a limb is obstructed and then released. He attributed the sensations to the thermal gradients set up when warm blood re-enters a cooled tissue. McGlone and I[11] however showed that such sensations could be intense when the limb was prevented from cooling, so that thermal gradients were absent or minimal. The stimulus is still likely to be a gradient, but it must be one of another type, possibly a chemical gradient, or one in osmotic pressure. One can therefore assume that thermal gradients in causing stimulation probably induce other gradients, and that these in turn stimulate nervous tissue.

Jenkins[13] has recently studied the effect of the shape of the applicator used as a stimulus on adaptation to thermal sensations. The time taken for adaptation depends on two factors: (1) the initial strength of the stimulus, and (2) an effect at the perimeter which varies with its length. These results may be interpreted tentatively in terms of a pseudo-reversible reaction $A \rightleftarrows B$ for cold, with a third substance, *C*, necessary for the recovery phase. The perimeter effect is ascribed to the diffusion of *C* inward from the surrounding tissue. A similar system is assumed for warmth. The data appear definite. Without denying a probable role of chemical changes in sensation, the perimeter effect seems to be more probably explicable as the result of thermal gradients generated by the entrance of warmer or cooler blood at the periphery.

McGlone and I[14] attempted to analyze our data on the prepuce in relation to its applicability to theories of stimulation. Analysis was somewhat precarious, so we tried to state the evidence conservatively. I wish to refer to this attempted analysis again now, if you will allow me, because my friends have told me that it would be well if I offered a translation of its unintelligible English into less unintelligible English. Hence in discussing the essential points I will try to make my errors in the opposite direction of over-confidence.

Evidence has been discussed which makes it improbable that the essential stimuli for thermal sensations can depend on either the temperature level or on the rate of change of temperature. Experiments on the prepuce such as those indicated in Fig. 1, *C* and *D*, lead to the same conclusion. For *C*, the stimulus was a metal applicator through which water at 18.2 °C circulated; the original difference in temperature between the skin and the applicator was 5.3 °C. For *D*, the original difference was 14.6°. Though the latter produced a more rapid change in temperature throughout the whole fold, it was a much less effective stimulus for sensation. The change in temperature required to induce sensation was much greater, the level reached much lower, regardless of the depth assigned to the receptor. If one assumes a receptor at a depth of 0.1 mm below thermocouple 1, one may estimate a thermal change of about 0.2° for the direct and one of about 1.2° for the reversed stimulation. Yet no such discrepancy is seen with direct and reversed stimulation by warmth. If the receptor is assumed to lie as indicated in Fig. 1, *A* and *B*, then the change in temperature required for stimulation by warmth was about 0.12° for *A*, and about 0.14° for *B*. These marked contrasts may be explained if a thermal gradient is considered as the factor concerned in stimulation.

It will facilitate discussion and make for clarity if the conditions are stated more precisely on a tentative basis, even though adequate data are not available. Something is known of the distribution of receptors in the thin skin of the prepuce, something of the thermal gradients in the thicker skin of the forearm; the general arrangement of the blood vessels is known for both. Consequently, the thermal

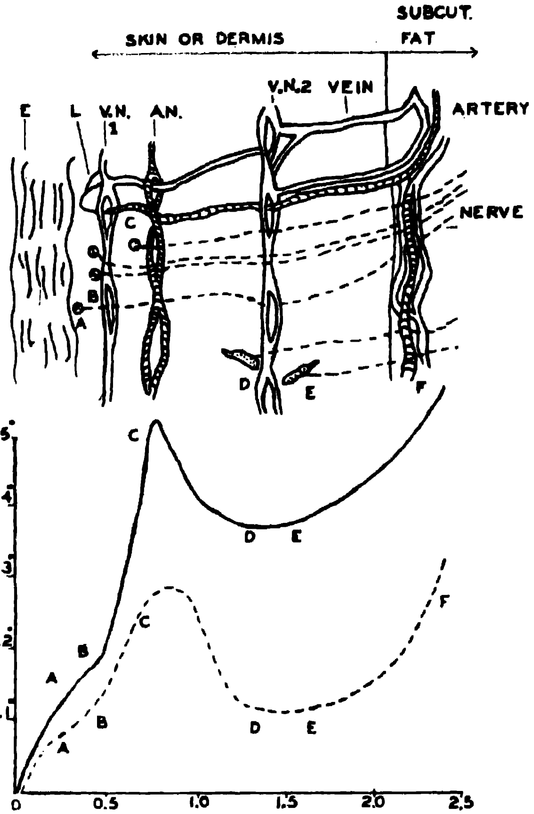

FIG. 3. A schematic representation of the normal resting thermal gradients in the skin of the forearm. Depths in man are shown as abscissae and differences in temperature from the surface temperature in °C as ordinates. The heavy line indicates conditions when the blood flow is rapid (skin hyperemic), the dotted line those where the flow is slow. Above, the probable positions of the arterial and venous plexuses described by Spalteholz are shown in relation to the thermal gradients. The arrangement of the vessels connecting the plexuses is shown (and that crudely) at the top of the diagram. Possible positions for cold receptors are *A*, *B*, and *C*, for warm receptors *D*, *E*, and *F*. The epidermis is indicated by *E*, the level of capillary loops by *L*, the more superficial venous net by V.N.1 and the deeper by V.N.2. A.N. is the arterial net or plexus. Nerve fibers are indicated by dotted lines. The thermal gradients shown are those determined experimentally except for the slight theoretical modification in the most superficial 0.5 mm that is discussed in the text.

gradients, the arrangement of blood vessels and the possible positions of the thermal receptors for the forearm are set forth in a crude diagrammatic fashion in Fig. 3. Beneath the non-vascular epidermis there is a system of capillary loops, and deep to this first and second venous networks (or plexuses) with an arterial plexus lying between them which is nearer to the first venous plexus than to the second. In this area the arteries and veins do not commonly follow similar paths. Deep to the second venous network within the skin or dermis, and still deeper in the subcutaneous fat, the veins commonly follow the arterial paths as venae comites, though they may have an independent course. In the forearm the thermal gradient is certainly modified by this arrangement of blood vessels, and it has approximately the form shown in Fig. 3. The peak of temperature at the level of the arterial net and the trough at the deeper second venous net are definitely established. The shape of the gradient between the arterial net and the skin is not exactly known, for here the character of the tissue changes rapidly within a distance of 0.1 mm and the exact form of the gradient cannot be determined. The gradients found experimentally[15,16] have here been slightly modified on the grounds of the probable effects of the anatomical structure. The exact depth of the Krause and Ruffini receptors in the skin of the forearm is not known, though Krause receptors are found quite superficially and Ruffini deeper in the dermis. By comparison with the prepuce material, the receptors for cold (Krause) are assumed to lie at *A, B,* or *C* (Fig. 3), with *B* the most probable. The receptors for warmth (Ruffini) are assumed to lie at depths *D* or *E,* with *D* slightly the more probable on physiological grounds. The gradient hypothesis will be discussed on the simple assumption that the receptors lie at levels *B* and *D* respectively, though in the case of warmth, additional receptors probably also exist at *F* or deep to *F.*

The thermal gradients in the skin are certainly modified according to the rate of blood flow. When the skin vessels are dilated and the rate of blood flow is fast, as it is in a warm environment or as the result of inflammation, the skin is said to be hyperemic, and the gradients are of the type shown in the heavy line in Fig. 3. When the vessels are contracted the gradients are less steep in the skin, but steeper than normal in the subcutaneous tissue (dotted line of Fig. 3). In the hyperemic skin it is more difficult to elicit cold sensations, easier to elicit warm; the threshold for cold has been raised, that for warmth lowered.

On this gradient hypothesis the receptors for cold and warmth lie at depths where the resting thermal gradients are opposite in sign. A cold stimulus, to be effective, has merely to exaggerate the normal gradient, and the same conditions hold for warmth. Whereas the cold receptor lies in an area with steep gradients, that for warmth is situated where the gradients are very flat. Cold can affect the body normally only from without; warmth may act from without or may be generated within the muscles. Since the skin is supplied by arteries which pierce the muscles, the warm receptors may also be affected by heat of muscular origin.

The conditions for stimulation by warmth would be as follows. The normal slight inversed gradients at *D* would be exaggerated by heat to the skin. Entrance of warm blood from the muscles to the arterial net would probably exaggerate the inversed gradient at *D,* and summate with any effect from the exterior. With stimulation of a double fold of skin, as in the prepuce experiments, the threshold change in temperature should not vary greatly with the direction of stimulation since the resting gradient is so slight. This is found to be the case. On the other hand, it should be very difficult to neutralize and reverse the normal resting gradient and cause paradoxical stimulation of warmth by exposure of the surface to cold. The difficulty of inducing paradoxical sensations of warmth is well known.* If the forearm were immersed in water at 36 or 37°, the deeper gradients for warmth sensation should at first be much exaggerated; later the temperature of the second venous plexus should be also raised, and a normal gradient be restored. Adaptation would have taken place. (Adaptation is here regarded as a peripheral mechanism dependent on the removal of a stimulating gradient. This may, or may not, be true for adaptation of other types of receptors.) If the forearm is immersed in water at 42 °C the gradients never return to normal, and adaptation does not occur. It is probable that rapidly flowing blood raises the temperature in the second venous net above that in the arterial net. The stimulating gradient of such maintained sensations is likely to be one opposite in sign to the resting gradient. If the forearm is moved from water at 42° to water at 41°, this abnormal gradient would be reduced to normal (for the temperature of arterial blood passing through the heated tissue probably exceeds 41°) and sensation temporarily disappears.

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* Cold receptors may readily be stimulated not only by cold but also by heat. Such induction of a cold sensation by heat is known as paradoxical stimulation. Similar paradoxical stimulation of warm sensations by cold, though much rarer, is also known.

With warmth the latency of sensation may be very long with stimuli of intermediate intensity. This is particularly seen in prepuce experiments where the conditions are somewhat abnormal through the excessive cooling of the stretched fold of skin. It may be noted in Table 1 that stimuli 10 to 13° above the skin temperature are often associated with very delayed sensations, whether the stimuli are applied in the normal or the reversed direction. With such stimuli the rate of change of temperature at the depth of the receptors is very different according to the direction of stimulation, so that these anomalous results are correlated with the rate of change near the surface stimulated rather than with those at the receptor level. The stimuli concerned are those just insufficiently warm to be called "hot" by the subject. These complexities are most readily explained as an interference phenomenon associated with mild simultaneous paradoxical stimulation of cold receptors. They do not invalidate the gradient hypothesis.

The conditions of cold stimulation are also readily explained. The cold receptor lies in an area with a steep thermal gradient. If this gradient is exaggerated by exposure of the surface to cold, stimulation results, with an over-all latency of 0.3 to 0.5 second. If a hot stimulus is applied to the skin, the receptor may be stimulated by a gradient of the opposite sign. Since the resting gradient has to be first neutralized, and then reversed, the latency of such paradoxical stimulation is much longer, namely, 0.7 to 0.8 second.[17] Similarly, with reversed stimulation of a prepuce fold (Fig. 1, *D*), the normal gradient has first to be neutralized, and the delay is even longer than with paradoxical stimulation of the surface, for the stimulus has to act on highly vascularized tissues of considerable heat capacity. It is obvious why the equation suggested for calculation of the depth of the receptor (an equation which assumes that the time taken in generating the stimulus is a constant) cannot work for a receptor situated in an area with such a steep thermal gradient. One difficulty in the gradient hypothesis lay in the fact that hyperemia of the skin raised the threshold for stimulation by cold, even though the steeper resting gradient (indicated in Fig. 3) should theoretically have rendered stimulation easier. Consequently, in the original report the theory was advanced that the stimulation might depend on chemical changes in the blood resulting from changes in temperature as it flowed across a thermal gradient. Rapid flow might then be a disadvantage. This would appear to be the readiest explanation if the receptors lie superficial to the vessels in position *A* (Fig. 3). If, on the other hand, they lie at *B* deep to many of the capillary loops, hyperemia with increased blood flow might actually decrease the resting thermal gradient in this precise locality. This has been suggested in the drawing of the curves of Fig. 3. The observed facts then fit the general hypothesis.

The mechanism of stimulation by a gradient is again merely a matter for speculation, speculation which is unwarranted except as a stimulus to experiment. One must remember that the actual anatomical arrangement is much more complex than that indicated in Fig. 3. The Ruffini end-organs are known to be surrounded by an elaborate network of small blood vessels; Krause's end-organs are said to have a capillary loop in close apposition to them.[18] Excitation of a nerve is induced by a depolarization gradient along its axis. It is possible that a receptor lying in a thermal gradient maintained by the arrangement of blood vessels might have changes in its membrane which lead to instability and cause it to fire repetitively. Nothing is known of the effect of temperature changes on tissue cells, but by analogy with conditions in the blood they may be considerable. For instance, a fall of temperature of 1 °C increases the pH of blood plasma by about 0.014, if the gas content of the blood is maintained constant, and such changes may be demonstrated *in vivo*.[19] Also a fall of temperature at constant pH of plasma decreases the difference in pH that normally exists between the plasma and the contents of the red blood corpuscle.[20] The real difficulty lies in finding any such mechanisms which might be sensitive to the minute alterations in thermal conditions which determine stimulation of thermal receptors.

The Mechanism in the Ray

The solution of the problem of the mode of stimulation would seem to lie in the investigation of isolated receptors such as those obtainable from the ray, as in Sand's experiments.[7] If the mechanism of a single thermal receptor can be analyzed, the clue may apply to all. The receptors in the ray lie close to the mouth and arising in these receptors there extend across the skin of the head long tubes several cms in length filled with a thick viscous jelly. The tubes open by small orifices on the skin surface through which the jelly may with difficulty be expressed. Excised receptors are sensitive to cold even if the jelly-like material is removed (as far as is possible) from the nervous tissue. The ray is often found in estuaries, where the water composition is variable, and it is possible that the receptors, though sensitive to temperature changes, function normally in detecting some other change (*e.g.*, osmotic). Sand interprets the sensitivity of the preparations to cold on the basis of the interactions of two processes, one of which rapidly attains a new equilibrium on exposure to a new temperature, and the other only slowly. The frequency of the impulses is assumed to be a function of the difference between the velocities of the two processes. These processes may be chemical reactions, changes in viscosity or the like, but "a conception of a time factor of kinetic equilibrium" is likely to be involved. I would like to end by pleading for continued study along these lines and the allied physicochemical problems. The field looks extremely promising.

Discussion

James D. Hardy: I think we are indeed fortunate to have Dr. Bazett present so thoroughgoing and up-to-date a treatment of temperature sense in man.

The classic work on the identification of the nerve endings responsible for heat and cold sensation by Dr. Bazett and his associates is well known to everyone interested in temperature sense. Their identification of the sense organs of temperature has been criticized because the Ruffini and Krause endings are found usually in the genital organs rather than widespread over the skin surface. I should like to ask Dr. Bazett why his technique could not be extended to the forearm, for example? A thin slice of tissue could be easily removed from the arm, surgically, after thorough mapping.

Dr. Bazett takes the point of view that the temperature end-organs are of service to the body mainly for avoiding local injury, that is, burning or freezing. It has been my feeling that this was a local function of the receptors but that their general function was regulation of heat loss and body temperature. I should like to know what Dr. Bazett thinks of the relationship between the thermal receptors and control of body temperature in man.

Reply

H. C. Bazett: There can be no doubt that the specific exposition of a gradient hypothesis here tentatively advanced is entirely unwarranted without further evidence, if such evidence can be obtained. There is no doubt that anatomical study of receptors should be extended to the forearm. While this is theoretically feasible, up to the present all attempts have failed. The difficulty lies in the fact that a comparison of the nerve elements with the sensory pattern gives no valid evidence unless all the receptors are consistently stained and identifiable. This has so far been attained only by the methylene blue method, a method which is very difficult to apply to tissue thicker than prepuce skin. Krause and Ruffini receptors are undoubtedly found all over the skin, but their exact distribution is not known. We attempted such a study in the forearm and several square centimeters of skin were removed from Dr. McGlone's forearm after careful repeated mapping with tattooing. The staining proved inadequate. I hope others may prove more successful.

As to the relationship of thermal receptors to heat regulation, I, of course, agree with Dr. Hardy. I would not distinguish between such a response and that to injury. Even moderate warmth or cold would be injurious, if reflex adjustments, brought about partly by thermal sensations, did not prevent such injury.

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A New Basis for Cutaneous Temperature Sensitivity

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According to the traditional view, the temperature sensitivity of the skin depends upon a relatively small number of warm and cold receptors per sq cm, corresponding to the warm and cold spots which are found when the skin is explored with a small stimulator at appropriate temperatures. The numbers vary, but average figures are 13-15 cold spots and 1-2 warm spots per sq cm.

The evidence for this doctrine of discrete spots is derived from single mapping with an all-or-none response. That is, the skin is explored only once, or possibly twice. The subject merely responds "cold," "warm" or "neutral" to each stimulation. Thus a map of the spots is obtained. If the location of some of the spots fails to correspond exactly when the mapping is checked—and this is usually the case—there is no way of telling where the trouble lies. It may be that the spots themselves are inconstant, or simply that the technic of mapping is inaccurate.

To obtain a more adequate description of the distribution of temperature sensitivity, a method of *seriatim* or repeated mapping is necessary. In the seriatim method, a checkerboard pattern is stamped on the skin and mapped in random fashion, not once or twice, but six or more times, with suitable rest periods between, to allow the effects of adaptation to wear off. Instead of a simple all-or-none response, the subject is trained to report in a graded series: 0 for neutral, 1 for weak, 2 for medium and 3 for strong (cold or warm, as the case may be). With six such mappings, we obtain six report numbers for each square of the checkerboard. By the convenient, although theoretically reprehensible, device of treating these ordinal numbers as if they were cardinal, we then secure a *score* for each square, merely by adding the report numbers. These scores may range from a minimum of "0" (six zeros) to a maximum of "18" (six threes).

There are several advantages of this seriatim method over the usual single-mapping technic. In the first place, it is possible to determine the *reliability* of the results, simply by correlating the scores from two sets of six mappings on the same checkerboard. Hundreds of such correlations have now been made. They leave little doubt as to the constancy of cutaneous temperature sensitivity under normal conditions. Even with untrained subjects, reliability coefficients of .80 or higher are obtained in more than half the cases, and figures of .90 or better are not uncommon.

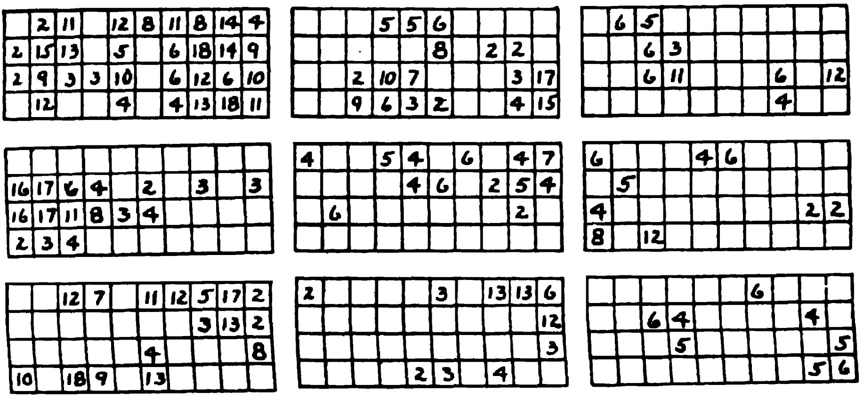
In the second place, the seriatim method can reveal *gradations* of sensitivity if they exist, instead of forcing an all-or-none description. Again, the evidence from a large number of subjects shows clearly that gradations of statistically reliable difference are present—in some cases, at least half a dozen steps. Finally, the influence of such factors as *size* and *temperature* can be studied by mapping alternately with two different sizes or two different temperatures.

From the preliminary research with this seriatim method, we may select two major findings which vitally affect the picture of cutaneous temperature sensitivity:

(1) The results fail utterly to substantiate the generally accepted doctrine of warm and cold spots. Several hundred mappings have now been made with stimulators varying in size from 3×6 mm down to 1 mm in diameter. Regardless of the stimulator size employed, the maps show one common feature. There are

always extensive *regions* of positive response—not separate spots. There are hills and valleys and plateaus, and an occasional steep precipice; but isolated positive squares, surrounded by zero squares, are conspicuously absent.

As an extreme example, Fig. 1 shows some maps made with a stimulator only 1 mm in diameter—the traditional size for mapping warm and cold spots. In spite of the small size, with the consequent difficulties of placement and reporting, the reliability coefficients for these maps are all .88 or higher, indicating very high consistency. Wide individual differences are apparent. The percentage of positive squares varies considerably. Yet, whatever their number, the positive squares are found typically in *clusters*, not singly, except at the edges where we do not know what lies beyond.



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				2	3		4		

						6			
		6	4					4	
			5						5
								5	6

FIG. 1.

With a stimulator 1 mm in diameter, we have about reached the limit of accurate manual placement. Mechanical stimulation might permit the use of still smaller sizes, if we could find some way of completely immobilizing the skin—no small task. This has not yet been attempted because there is no reason to expect that we could thus resolve the clusters into their ultimate components. It appears that we are faced with a definite limit to the *resolving power* of mapping. Our results indicate that, as the stimulator size is progressively reduced, the clusters simply disintegrate without being resolved. We may finally reach a stage where only a single tiny point remains responsive out of an originally large cluster. But this is not resolution. This single point may mark the highest peak of sensitivity, but it is no more descriptive of the *topography* of the region than the single church spire which remains visible above flood waters.

What about the traditional warm and cold spots? It appears that they are merely the artifacts of an inadequate method of mapping. Seriatim mapping does not confirm their existence. There is no reason to suspect that they actually mark the locus of individual warm and cold receptors. In fact, it appears that the delimitation of individual receptors may lie beyond the resolving power of any kind of mapping. For the present, at least, we must conclude that the temperature sensitivity of the skin is not *mappably* punctiform.

(2) It is still possible, however, that each *cluster* represents a unit corresponding to a single receptor, the surrounding gradations being due to differential transmission of temperature changes to that receptor. Fortunately, this hypothesis is

open to a direct experimental test. If differing scores on two adjacent squares, for instance, are caused by differential transmission to a single receptor, a stimulator which covers *both* squares should give a score at least equal to the *maximum*. The receptor could not be less strongly stimulated by a larger stimulator.

Fig. 2 shows the critical results. The figure combines a large number of instances where the same area has been mapped with two different sizes, and the corresponding whole and part scores compared. The ordinates are part scores, the abscissae whole scores. The basic curve is plotted from cases where the two part scores have identical values and provides a basis for comparing various functions. A, B, and C show various functions of the part scores where these differ by 4 or more units. Clearly, the third function (square root of the mean of the squares) provides the best fit. From the standpoint of our problem, however, the important point is that the *maximum* does not fit. The whole scores are consistently *less* than the maximum of the part scores. In terms of the transmission theory, this is impossible. Hence, the theory must be false. Variations of sensitivity within a cluster cannot be accounted for in terms of differential transmission to a single receptor.

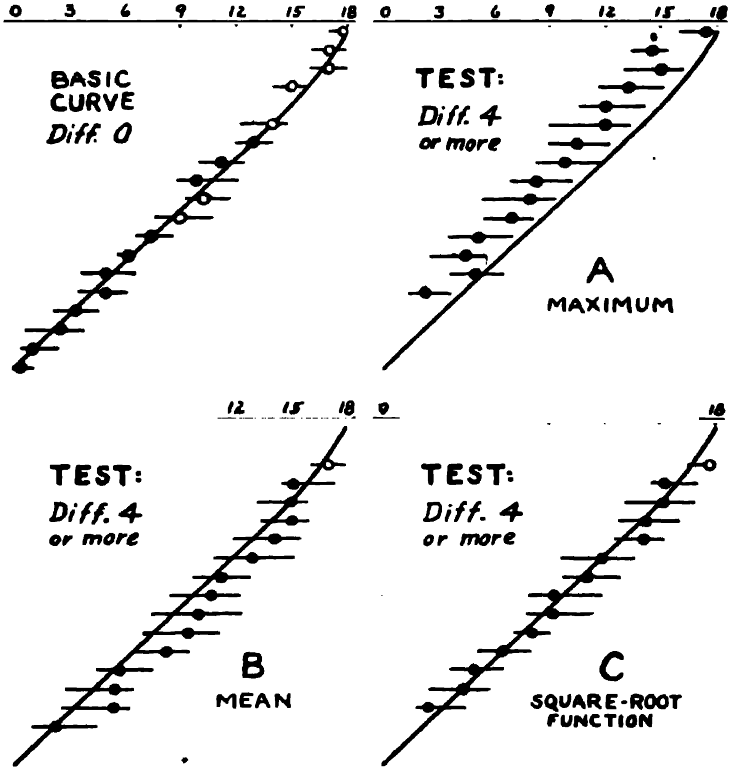

Fig. 2.

What, then, is the basis of cutaneous temperature sensitivity? It is clearly non-uniform, yet neither mappably punctiform nor dependent upon variations in thermal conduction. Let us assume that there are a great number of minute warm and cold receptors, so many and so small as to lie beyond the resolving power of our mapping technics. Let us assume that the variations in sensitivity are caused primarily by the *concentration* of these tiny receptors. Where cold receptors are densely packed, we have high sensitivity to cold. Where warm receptors are numerous, there is high sensitivity to warmth. Where either kind is very sparse or absent, there is correspondingly little or no response to that type of stimulation. The theory is crudely represented by the shaded maps of Fig. 3, derived from the scores previously shown in the maps of Fig. 1. Deeper shading indicates a heavier concentration of receptors.

This, in essence, is the *concentration theory* which is proposed as a new basis for cutaneous sensitivity to warm and cold. Many details remain to be worked out, although research now in progress is clarifying some of the essential relationships. In any event, as a working hypothesis, it provides a better theoretical framework for the experimental facts than the traditional doctrine of warm and cold spots.

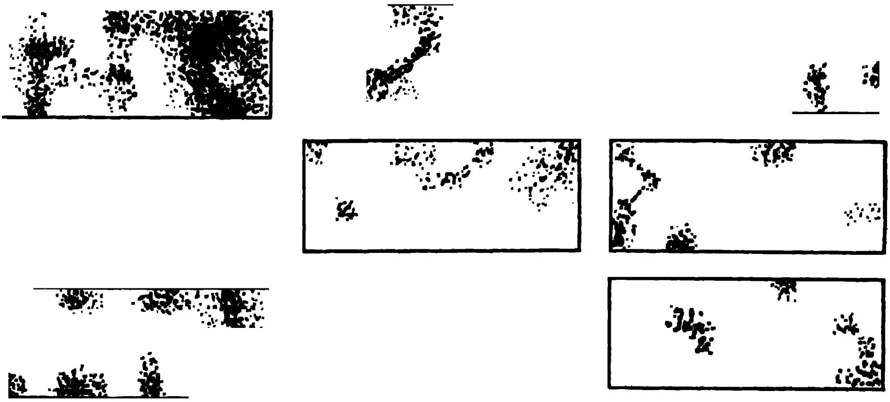

FIG. 3.

Discussion

A. P. Gagge: A detailed description of the technic of mapping should be given, stating the size of the checkerboard, location of skin area used, and position of subject during course of test. The temperature of the various stimuli should be stated as well as any other technical data that would clarify the various sensory tests. A clearer description of seriatim method should be given. It should be shown what sort of results are to be expected by the method if the traditional warm and cold spots actually exist. The deduction that there are no punctiform hot and cold spots should follow from the failure to observe the ideal seriatim plot. If the concentration theory is a reality, a criticism of known anatomical and histological studies should be given, showing why such a concentration of hot and cold spots have not been observed up to the present date. A more formal statement of this new theory would be a definite contribution to the proceedings.

L. P. Herrington: Many items of information necessary to a critical review are omitted, such as the size of the skin squares, the temperature of the stimulators, and the method of stimulator application, etc.

It is not clear as to what the plots and scores represent. Do they deal only with warm responses, only with cold responses, or with a combination of the two?

Does a positive score mean either hot or cold? How were the correlation coefficients used to estimate reliability computed? If they included hot, neutral, and cold responses, it is difficult to see what meaning a square score has in terms of sensation. If the square score deals only with one category of sensation, as seems probable, what kind of distribution obtained? In the nine rectangles of Fig. 1, about 230 out of 360 squares have zero response, and it would seem that a correlation between successive runs or the means of two sets of six runs would be influenced chiefly by the reliable *absence* of sensation in over two-thirds of the area tested.

If the argument against punctiform distribution based on the smaller scores found with the larger stimulator is accepted at face value, it is difficult to see why a "concentration" hypothesis avoids the same difficulty in interpretation. In fact, it seems likely this comparison has no bearing on the transmission question, but reflects instead some unknown effect not concerned with temperature which influences the report; possibly the smaller stimulator results in a higher percentage of reports which confuse touch with the lower grades of thermal sensation.

The author's density maps probably reflect the subjective experience accurately, but whether they indicate the gradations in statistical certainty of a sensation around a single receptor as influenced by transmission factors, or gradations in the concentration of receptors, cannot be judged on the basis of the experimental information included in the report.

H. C. Bazett: The difference between the technic employed by Dr. Jenkins and that used by myself and my collaborators is perhaps not as great as it seems. In mapping for cold spots we also stamped a grid (1 cm ruled in mm) on the skin. We explored the points repeatedly and allowed at least 5 minutes between individual stimuli for the final critical stimulations. The main difference is that we merely noted the points of most acute sensation in any sensitive area and considered these the cold or warm spots. We considered it impossible to prevent spread of thermal effects, and so believed lesser grades of sensation to be due to spread to the adjacent more sensitive spots. The single mapping described by Dr. Jenkins as used by others does not apply to our work. The essential and important finding by Dr. Jenkins is that the conscious sensation elicited from stimulation of an area may be less than that aroused by similar stimulation of the most sensitive part of it. This fact does not disprove von Frey's classical theories, though these theories will need to be adapted to fit the new facts. Unless this is shown to be impossible, the balance of evidence, I believe, still favors the older theory.

I would welcome a more complete statement of methods used by Dr. Jenkins for obtaining data as well as the analysis of the data. Unless I had read previously several of his papers, I should have been unable to grasp his method of analysis. In particular the time elapsing between successive stimuli of the same point should be stated, as the residual temperature changes following stimulation may last many minutes.

James D. Hardy: It is indeed fortunate that we have had presented to us today discussions of the modern concepts of temperature sense by a physiologist and by a psychologist. The two points of view, although widely separated, must agree before the problem of temperature sense is adequately understood.

There can be little doubt that Dr. Jenkins has made the most precise mappings of local areas to determine the sites within those areas which are most sensitive to hot and cold stimuli. Further, one must accept the fact that a large-area stimulator, used under his conditions, produces less effect in producing temperature sensation than the small-area stimulators. These appear to be the facts in the case, from which Dr. Jenkins concludes that the older views of von Frey, Strughold, and Bazett are wrong, *i.e.*, the Krause and Ruffini nerve endings are not the specialized endings responsible for cold and heat sensations respectively. Dr. Jenkins would rather blame the undeveloped free nerve endings, which already have such a load of various sensations, from light touch to pain, that the addition of heat and cold does little but say that the anatomical basis for cutaneous sensation is far from satisfactory. Until the technic of Bazett and his associates has extended to other parts of the body, the concentration theory must wait for its final acceptance.

Dr. Jenkins' facts are entirely to be expected from Bazett's work. That is, one should never be able to "resolve" the clusters found by Dr. Jenkins, because heat will be conducted from the precise point of stimulation several mm in all directions. As it requires less than 0.06 °C change in skin temperature to evoke a sensation from an end-organ, stimulation with a copper point several degrees below or above skin temperature will have quite a widespread influence. Therefore, all the mappings of Dr. Jenkins can be accepted without the necessity of further theories as to end-organs.

The most unexpected finding which Dr. Jenkins reports is that a stimulator 1×2 mm in area has less effect than that of the usual area, 1 $mm,^2$ in two adjacent spots. That is, we are faced with an actual inhibition effect no matter what theory we use. This is an entirely new effect, and its cause can only be speculated upon. It is worthwhile suggesting that the inhibition may result from stimulation of touch. This suggestion can be tested experimentally by using radiation as a stimulator.

Reply

Dr. Bazett, Dr. Gagge, and Dr. Herrington have all raised questions regarding the technic of seriatim mapping which I will attempt to answer by giving additional information which could not be included within the limitations of a fifteen-minute paper.

The maps consisted of 50 squares varying from 1 × 1 to 3 × 3 mm, depending on the size of the stimulator used. This pattern, 10 × 5 squares, was stamped transversely on the volar surface of the left forearm about midway between the elbow and wrist. The subject was seated with the arm resting on a sponge rubber pad.

The data reported in this paper were all obtained with cold (17 °C). Two subjects were mapped alternately with a uniform time of three and one-half minutes for each, giving an average of seven minutes for recovery between mappings of the same squares. Similar mappings have been made with warmth (44 °C) with three subjects working in rotation, requiring five minutes each and allowing an average of fifteen minutes between successive mappings. These time intervals were adopted after considerable preliminary testing to determine what time was necessary to prevent any noticeable effects of adaptation on the magnitude of the scores. Specifically in reply to Dr. Herrington: warm and cold were always mapped separately and the term "positive report" in the data cited refers only to cold. Similar results have also been obtained with warmth. Comparative mappings have been made with various other temperatures besides 17 °C and 44 °C, but these were not reported at this meeting.

Correlations between two sets of scores to determine reliability are carried out by the product-moment formula. While a single figure, such as the coefficient of correlation, scarcely gives a completely adequate description of a subject's consistency, it provides a simple method of eliminating those results in which inconsistent reporting might obscure the relationships.

The problem of the spread of stimulation is one on which we need more direct evidence. In the absence of this, it seems rather pointless to argue on logical grounds. It is my opinion, however, that this explanation for the clusters of squares of varying scores is not a very hopeful way to attempt to solve this problem. It should be kept in mind that the actual period of contact of the stimulator with the skin for cold stimulation was approximately one second. Repeated tests have shown that it is rarely possible to get any sort of a positive response out of a consistently zero square no matter how long the stimulator is held in place.

The chief argument at present against such an explanation lies in the data already presented. It has been pointed out that when two squares of different sensitivity are stimulated simultaneously the score is *less* than the maximum of the parts. As I see it, this absolutely rules out the possibility of the "spread" explanation, unless it can be shown that the reduced total score is the result of some artifact. I am still open to conviction that some artifact is present. However, *tactual interference* (suggested by Dr. Bazett, Dr. Hardy and Dr. Herrington) will not do. If tactual interference explained the reduction, it should occur regardless of the relative magnitude of the temperature experiences, but if two squares have *identical* seriatim scores and are stimulated simultaneously, the total score is not less than the parts but actually slightly greater. Hence, it follows that tactual interference is not the correct explanation.

Dr. Gagge raises the question of what the seriatim maps should look like *if* the traditional spot theory is correct. With subjects who give reliability coefficients of .90 or better, there should be numerous isolated positive squares surrounded by "zero" squares. The maps from such subjects already presented show very clearly that the positive squares always occur in clusters. Hence, there is no direct evidence of warm and cold spots from these seriatim maps. To assume that each cluster represents a spot requires the assumption of thermal-transmission to explain the surrounding gradations. This has already been shown to be inadequate.

In answer to Dr. Hardy, I am as much concerned as he is with the problem of assigning still more functions to the so-called free nerve endings. However, I am disturbed even more by the assignment of temperature sensitivity to capsulated receptors (like the Krause and Ruffini endings), because these have not been demonstrated histologically to be present throughout the skin generally.

Dr. Herrington has requested a more formal statement of the concentration theory. At present I feel that the evidence does not justify our viewing this as more than a provisional working hypothesis. My chief interest is in showing that the traditional theory is inadequate, thus directing attention to the need for *some* new basis for cutaneous temperature sensitivity.

Man's Heat Exchanges with his Thermal Environment

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The poets have defined man in highly varied terms, from "the interpreter of God," and "a reasonable being," and "a thinking creature," through "a tool to buy and sell," "an ape and an angel," to "a two-legged animal." All these characteristics, and many more, may be justified. In the booth of the Committee on the Hygiene of Housing at the New York World's Fair, one exhibit is headed "Man is a Heat Machine." This description is, perhaps, more fundamental than any of the others and is, at any rate, basic for the present discussion.

Heat Production in the Body

All the activities of living things are dependent upon the fundamental processes of tissue-oxidation which we group under the name *metabolism*. The gross energy equivalent of these processes is measured by a standard physiological procedure involving the direct determination of the oxygen consumed when the subject breathes air from a closed circuit.

The extent of metabolism is expressed in Calories per hour of heat liberated by the observed consumption of oxygen; and variations in such heat production have been exhaustively studied by physiologists for many years. Metabolic rate varies with the size and shape (most closely with the surface area) of the subject, with age and sex, with physiological make-up and health, with diet and—above all—with muscular activity. The total Calorie production may range, for a man of average size, from 60 Calories per hour in sleep to 600 Calories per hour in strenuous exercise.

Avenues of Heat Loss from the Body

This considerable and highly variable amount of heat energy is partly used up in external work. The residue must be dissipated from the body almost as rapidly as it is produced in order to avoid over-heating of the body tissues which, if in excess of some 5 °C, may prove fatal. On the other hand, if heat is removed from the body at a rate in excess of metabolic heat production, equally serious results may ensue, although the limits on this side of the thermal scale have not been so closely defined.

The processes by which heat is given off from the human body are, therefore, of basic importance. There are five processes involved which are fundamental. Heat is constantly being produced by metabolism. Heat is constantly being lost by evaporation from the body surfaces. Heat is constantly being lost by convection to the ambient air, if that air is below the temperature of the skin, or gained, if that air is above the temperature of the skin. Heat is constantly being lost by radiation to surrounding surfaces if those surfaces are below the temperature of the skin, or gained from those surfaces if they are above the temperature of the skin. Finally, the net arithmetical difference between these four processes must be registered by a change in the mean temperature of the body tissues, which we have called storage, and which we define (for the subject at rest and performing no appreciable amount of external work) by the equation:

$$M - E \pm C \pm R = S.$$

The "heat loss" factors in this equation have been much less fully studied than the "heat production" factor of metabolism. Rubner (1896) made a rough theoretical partition of the avenues of heat loss, and Aldrich (1928) first measured radiation loss with some accuracy. The excellent work of Houghten, Teague, Miller and Yant (1930) first established a partial partition over a considerable range of atmospheric conditions but did not distinguish between radiation and convection. Bohnenkamp (1931) studied radiation in detail but estimated both convection and evaporation. Only during the last five years have reasonably adequate data become available through work carried on at the Russell Sage Institute of Pathology in New York by DuBois and Hardy, and at the John B. Pierce Laboratory of Hygiene in New Haven.

Methods of Partitional Calorimetry

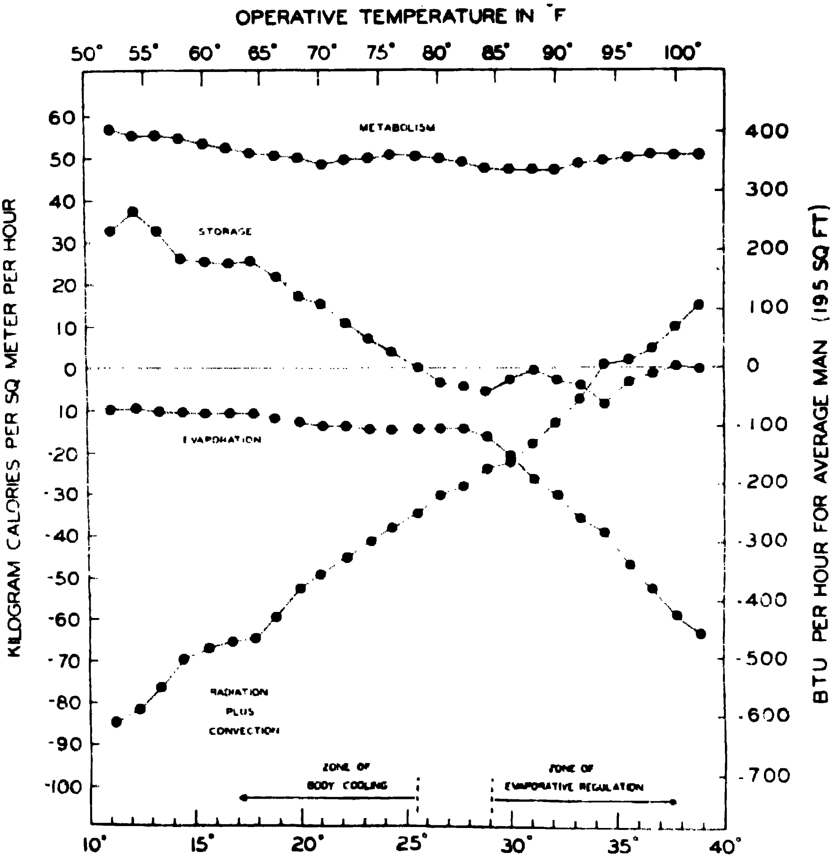
The studies in our own laboratory (Winslow, Herrington, and Gagge, 1936) have been directed to a complete analysis of the five factors of heat interchange, carried on simultaneously and representing cross-sections of physical processes and physiological adaptations at relatively definite periods of time and extended under comparable conditions, over a wide range of variations in all the external physical factors involved. The procedure employed, which we have called Partitional Calorimetry, involves the observation of human subjects (so far, only young, healthy males) clothed or unclothed, at rest in a semi-reclining posture. In these experiments, we have made no attempt to maintain strictly basal conditions. A high degree of regularity in the living habits of subjects and the control of such factors as posture, activity, and irregular consumption of food has made it possible to obtain, from trained subjects, figures for "standard" metabolism which are consistent and show no greater statistical variability than that displayed in basal measurements. The subjects are placed in a specially constructed booth in which the temperature and humidity of the air can be accurately controlled by conditioning apparatus of the ordinary type but of a high degree of accuracy (well within 1 °C in temperature and 5 per cent in relative humidity). Radiation from the walls of the booth can be varied over a wide range, either by reflection from copper surfaces (in one booth) or by circulating steam or brine through the walls (in another booth). With the conditioned air supplied to a double shell space surrounding the booth itself, air movement can be cut down to less than 4 centimeters per second; and any desired higher degree of air movement can be produced by regulated propeller fans installed in the booth itself.

The procedure outlined gives us results which are quantitatively less accurate—in a single experiment—than those obtained by the standard methods of direct calorimetry. On the other hand, the ease and rapidity of observation makes it possible to control, by repetition and averaging of results, any errors involved. The method is highly flexible and specially adapted to the analysis of radiation interchange and study of the influence of air movement. Furthermore, it makes it readily possible to obtain a cross-sectional view of the processes of physiological response at any given time period of the adaptive process.

The methods by which external conditions are measured and by which values for each type of heat interchange are observed will be discussed in succeeding paragraphs. It may be pointed out here, however, that since we are dealing with a closed thermal system it has always been possible, when four factors are known, to estimate the fifth factor by difference—a procedure which has proved of inestimable value in deriving fundamental constants.

Avenues of Heat Loss Under Varying Environmental Conditions

The general phenomena of heat interchange in environments of progressively varied Calorie demand are illustrated graphically in Fig. 1. In this diagram, convection and radiation effects are combined, and each of the four factors (metabolism, evaporation, convection plus radiation, and storage) is plotted against "operative temperature," a figure which represents the combined effect of air and wall



Relation of metabolism, storage, evaporation and radiation plus convection to operative temperature. Lightly clothed, semi-reclining subjects. (Storage represents net change in temperature of the body tissues; under the convention used, a positive value for storage indicates cooling of body tissues. a negative value heating of body tissues.)

temperatures properly weighted to represent their respective physical influences upon the body. According to the convention we have used, storage is plotted as positive when it represents net loss of heat by the body or cooling of the body tissues. Thus, metabolism plus positive storage (above the zero line) equals evaporation plus radiation plus convection (when both are below the zero line). Data refer to lightly clothed, semi-reclining subjects.

At about 30 °C, some 50 kilogram-calories per square meter of body surface per hour are produced by metabolic processes under the standard conditions of diet and posture set for our subjects; and half of this heat is given off by evaporation, half by convection plus radiation. At lower environmental temperatures, evaporation decreases slightly, but heat loss by convection plus radiation increases rapidly as operative temperature falls, with a consequent rise in storage. Thus, at 15 °C, metabolism is about 55 kilogram-calories per square meter per hour, while evaporation accounts for 12 kilogram-calories and convection plus radiation for 68, leaving 25 kilogram-calories for storage or cooling of body tissues. This region of the graph we call the Zone of Body-cooling. At temperatures above 31 °C, heat loss by convection plus radiation decreases and above 34° becomes a positive heat gain, being balanced by progressive increase in sweat secretion and evaporative heat loss. Thus, at 38°, we have a metabolism of about 50 kilogram-calories, balanced by an evaporative heat loss of 60 kilogram-calories, with no storage plus a gain of 10 kilogram-calories from air and walls. This we call the Zone of Evaporative Regulation.

It is clear that general statements with regard to the proportion of heat given off from the body by various avenues have meaning only within a narrow range of environmental conditions. In the middle zone of optimum physiological adjustment (with air and walls of equal temperature) metabolic heat may be given off about one-third each, by evaporation, by radiation, and by convection. If the walls are much hotter than the air, however, radiative heat gain may balance convection heat loss, and only heat loss by evaporation remain to balance metabolism. With both air and walls above skin temperature, evaporation alone may balance metabolism plus heat gain by both convection and radiation.

With this preliminary picture in mind, we may now proceed to a consideration of the determination of each of the four major factors in heat interchange (considering metabolism as given) and of the various measurements which make such determinations possible.

Evaporative Heat Loss

As noted above, evaporative heat loss is determined directly by the decrease of weight of the subject as determined by a delicate platform scale sensitive to 2 grams, corrected for the weight difference of the O_2 and CO_2 components of respiratory exchange. The rate of evaporative loss is governed by the extent of moisture on the skin produced by sweat secretion; by the vapor pressure of this moisture (as determined by skin temperature); by the vapor pressure of the atmosphere (as determined by temperature and water content of the air); and by the rate of air movement. All these factors, except the amount of sweat secretion, can be directly determined, and from them the rate of effective sweat secretion can be computed.

Evaporative heat loss from the nude, semi-reclining body may be as low as 6-8 kilogram-calories per square meter of body surface per hour at low air temperatures, more than half of this evaporation deriving from the respiratory tract and less than half from the external skin. On the other hand, we have observed at high temperatures total evaporative cooling rates of over 59 kilogram-calories per square meter per hour, of which 55 calories were accounted for by evaporation from the skin (Winslow, Herrington, and Gagge, 1937).

Convective Heat Interchange

The determination of convective heat interchange must be made by an indirect procedure. The process is governed by the following equation:

$$C = K_C\sqrt{V}\,(T_S - T_A),$$

where C = convection loss in kilogram-calories per hour,

K_C = a constant depending on the physical processes involved and on the shape and posture of the individual subject,

V = velocity of air in centimeters per second,

T_S = mean temperature of body surface in centigrade degrees,

T_A = air temperature in centigrade degrees.

The value for K_C must be determined for an individual subject in a given posture by varying air temperature, with wall temperature and atmospheric humidity and air movement held constant, and operating within the zone in which storage is zero (Gagge, 1936). The general range of values for this factor may be illustrated by the fact that a stout subject weighing 230 pounds has a K_C of 2.30, and a slender subject weighing 105 pounds has a K_C of 1.87, both nude and in semi-reclining position (Winslow, Herrington, and Gagge, 1937). With still other subjects, values as low as 1.58 and as high as 2.52 have been obtained. Roughly speaking, then, if one could have an air velocity as low as one centimeter per second, the body would lose by convection two kilogram-calories for every centigrade degree difference in temperature between skin and air. Actually, what we

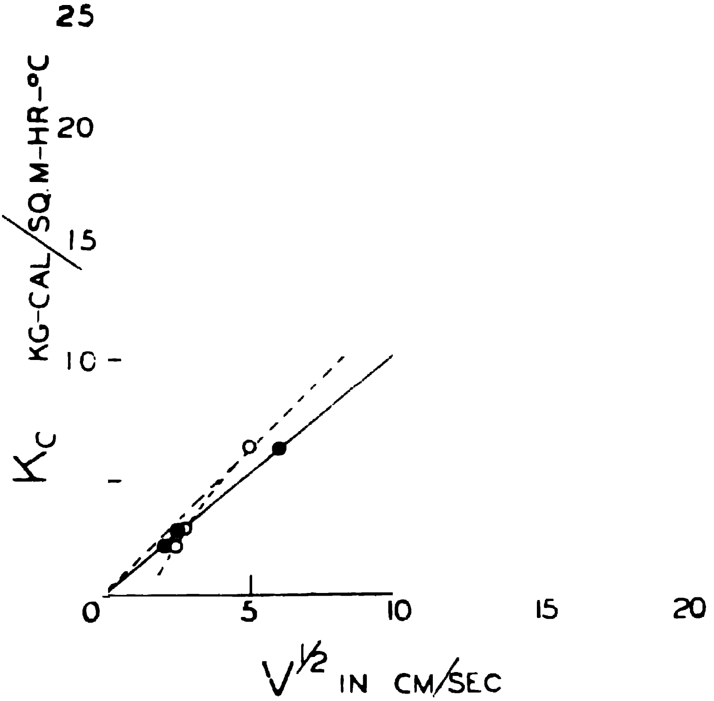


FIG. 2. Relation between total convection constant (K_C) and air movement. Solid circles for air velocities measured without the subject in the booth, open circles for air velocities measured with subject in the booth. (Winslow, Gagge and Herrington, 1937.)

ordinarily call "still air" has a velocity of at least four centimeters per second, so that the minimal value for $K_C\sqrt{V}$ is about four (Gagge, Winslow, and Herrington, 1938).

The assumption that moving air increases convective heat loss from the body in proportion to the square root of its velocity was merely an assumption at the beginning of our studies. Recently, we have demonstrated the validity of this relationship for velocities up to 264 centimeters per second (Winslow, Herrington, and Gagge, 1939), and have shown that the measurement of air velocity, by a hot-wire anemometer, can best be made without the presence of the experimental subject and at such a distance from the observer as not to be influenced by his body. Low initial air movements are increased by the presence of the experimental subject as a result of induced currents due to the warmth of the body. High initial air movements are reduced by the physical obstruction of the body. The use of air movements actually observed near the body of the subject, as influenced by these processes, yields results which are less consistent than those obtained by computation based on initial air velocities unaffected by the subject himself (Fig. 2).

The mean skin temperature of the subject has been determined in our studies by the use of a commercial modification of the Hardy radiometer (Hardy, 1934). In the case of the nude subjects these observations are made at three points on the head, three on the upper extremities, four on the trunk, and five on the lower extremities. The means for these four respective general areas are weighted in the ratios of 7: 21 : 31 : and 41 (following DuBois and DuBois, 1916) to obtain a mean T_S value for the body as a whole (Winslow, Herrington, and Gagge, 1936). In the case of a clothed subject, two of the observations on the upper extremities and all those on the trunk and lower extremities are made on the surfaces of the clothing. Observed variations in mean skin temperature will be discussed in a succeeding paragraph.

Air temperature has been continuously recorded by a Leeds and Northrup recording potentiometer.

In our experiments, we have observed convection losses in cold air of over 84 kilogram-calories per square meter of body surface per hour for our heaviest subject.

Radiative Heat Interchange

Radiative heat interchange is determined by four factors: the radiation characteristics of the body concerned, its radiation area, its surface temperature, and the mean temperature of surrounding surfaces. Under the conditions of our experiments, with walls emitting only low-temperature radiations of a wave-length beyond 10 μ, the absorption of either the nude or the clothed body may be taken as complete. Angle factors may also be disregarded under the conditions of our experiments (Gagge, 1936). Under these conditions total radiations may be computed from the Stefan-Boltzmann formula,

$$R = A_r K_r (T_S^4 - T_W^4),$$

where A_r = effective radiation surface of the body in square meters,

K_r = the universal radiation constant (4.92×10^{-8} kilogram-calories per square meter per hour),

T_S = mean temperature of body surface in Absolute degrees,

T_W = mean equivalent radiation temperature of surrounding environmental surfaces in Absolute degrees.

The surface temperature of the body is determined as described above; and the mean equivalent temperature of surrounding surfaces is determined by surveys with the radiometer, or, when checked against such surveys, by the collection of representative radiations on a reflecting copper hemisphere and the observation of the radiant temperature of that surface, or by the observation of heat absorbed by a special blackbody, the thermo-integrator (Winslow, *et al.*, 1935), after correction for convection interchanges.

The previously uncertain factor in this equation has been the radiation area, A_r. This factor has been determined in two ways. By holding air temperature, air movement and atmospheric humidity constant and working within the region of minimal storage where this factor is measured with reasonable accuracy by changes in rectal temperature, one can plot $M \pm S - E$ against varying values for T_W, and the slope of the line will give the effective radiation area of the body, under the conditions of the experiments (Fig. 3). The linearity of the results validates the conclusion (Gagge, 1936).

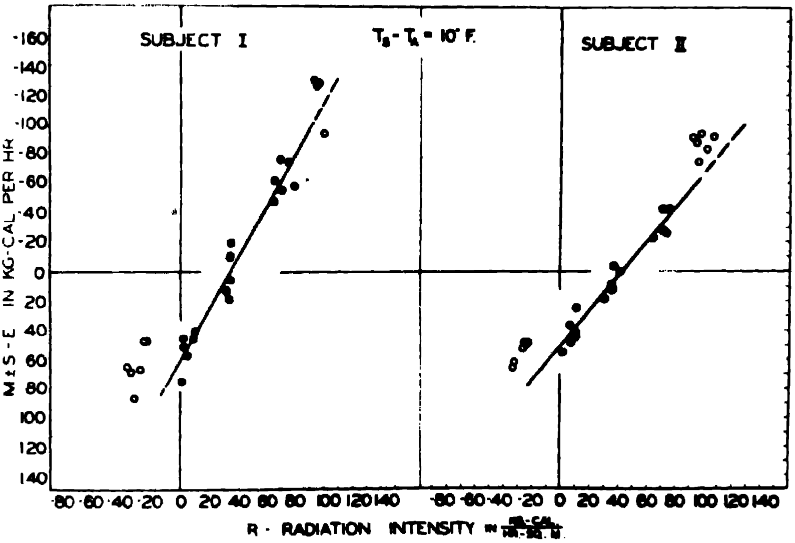


FIG. 3. Relation between radiation intensity and the arithmetical sum of metabolism, storage and evaporation, which must equal the sum of radiation plus convection. (Gagge, 1936.)

Again, by holding air and walls at the same temperature, but varying air temperature and air movement one may determine an over-all environmental constant (K_0), which represents the heat loss by radiation plus convection for each degree difference between body surface temperature and environmental temperature, and plot these K_0 values against air velocities. The slope of the resulting graph gives a value for K_C (the convection constant), and the ordinate intercept (since radiation is uninfluenced by air movement) gives us a measure of the effective radiation area (Winslow, Gagge and Herrington, 1939). Points at the extreme left are off the curve because storage is greater than that recorded by rectal temperature. Points at the extreme right fall off the curve because sweat is running off without evaporating.

Results obtained by these two independent methods check satisfactorily and show that, for the human body in a semi-reclining position, the effective radiation area is between 71 and 76 per cent of the total surface area of the body as determined by the DuBois formula, the slight variations being probably due to difference in the actual posture assumed.

In our experiments we have observed total radiation losses to cold surrounding surfaces as high as 40 kilogram-calories per square meter per hour and actual total radiation gains from hot surrounding surfaces as high as 90 kilogram-calories per square meter per hour.

Storage

Storage can be measured by changes in rectal temperature, when a rise or fall in the heat content of the body tissues is slow and no marked changes in blood distribution have taken place. Rectal temperature is observed by a thermocouple inserted for a distance of 6 inches beyond the anal sphincter. Gagge (1936) has demonstrated the validity of this procedure for the zone in question by the linearity of the derived relationships between $M \pm S - E$ and R.

For conditions in which heat content of the tissues and blood distribution change more rapidly, it is necessary to take account of skin temperature as well as rectal temperature. In recent studies, under cool environmental conditions (Winslow, Gagge, and Herrington, 1939), we have computed storage from a value for change in total tissue temperature obtained by adding the change in skin temperature to twice the change in rectal temperature and dividing by three. This procedure was validated for the conditions of our experiments by the concordance of the results obtained. Where all other avenues of heat interchange can be accurately evaluated, storage can, of course, be obtained by difference.

We have recorded actual storage ranging from negative values (heating of body tissues) of 10 kilogram-calories per square meter per hour to positive values (cooling of body tissues) of 59 kilogram-calories per square meter per hour (Winslow, Herrington, and Gagge, 1937).

Most of the data cited above (except those presented in Fig. 1) refer to the nude subject. Subjects under comparable conditions but lightly clothed, with a two-piece suit of cotton underwear, a cotton shirt, socks, low leather shoes, and a dark gray single-ply suit with three-quarter-lined coat and fully lined vest, have also been studied (Gagge, Winslow, and Herrington, 1938). The protection afforded by such clothing increases tolerance toward cool conditions by an amount equal to a 4 °C rise in air temperature. Its influence in the hot zone will be discussed in a later paragraph.

In all these processes, the body plays by no means a passive role. It has at least three adaptive mechanisms by which it modifies the influence of the physical environment; and, while our work has been primarily concerned with the basic physical factors of heat interchanges, a complete partition of such interchanges has thrown much light on the physiological processes of adjustment.

Physiological Control of Peripheral Blood Flow

The most obvious change in the body on exposure to cold conditions is a fall in skin temperature. This is passively influenced by changes in total tissue temperature (storage); but much more by alteration of the distribution of blood as between the superficial and deeper tissues. Mean skin temperature of clothed subjects may drop in the zone of body-cooling about 1° for every 2° decrease in external temperature. Wide variations occur on various areas of the body, the trunk surface varying least and the extremities most. Local stimulation of one area may cause enormous change in other areas. Thus, in one experiment, the application of a small ice-bag to the back of the neck for 15 minutes caused a drop in skin temperature on the finger of 10 °C, and this low finger temperature continued for one hour after the ice-bag was removed (Winslow, Herrington, and Gagge, 1938).

The various available methods of measuring skin temperature, and the literature on the relation of skin temperature to environmental temperature have been admirably reviewed by Murlin (1939) who gives a most helpful schematic analysis of the various factors at work.

It is of interest that the reaction of the body to air temperature appears somewhat greater than to wall temperature. If we compare two environments of equal total Calorie demand, one with air and walls of equal temperature and the other with colder air and warmer walls, mean skin temperature will fall more rapidly in the latter case than in the former (Herrington, Winslow, and Gagge, 1937; Winslow, Herrington, and Gagge, 1938). This phenomenon is probably due to the influence of cold air on heat loss from nose and throat and to conduction through the metal supports of the chair (Winslow, Gagge, and Herrington, 1940).

The degree of constriction of peripheral blood vessels in the zone of body cooling is a physiological phenomenon of major importance. Its effects have been extensively studied by Kleiber (1932, 1937) in animals, and by Bazett and McGlone (1927), Bazett and Burton (1935), Burton and Bazett (1936), and more recently by Hardy and DuBois (Hardy, 1934; Hardy and DuBois, 1937, 1938). As an index of variations in peripheral blood flow we may use a factor called conductance, suggested by the work of LeFevre (1911) and first fully developed by Burton (1934). In our studies we have determined this factor as follows: the sum of metabolism plus storage divided by surface area of the body gives us the heat flux per unit area of skin under given conditions; and this heat flux divided by the difference between skin temperature and rectal temperature gives the heat flux per unit gradient drop in temperature, or conductance. Total conductance is made up of specific conductivity of the body tissues and of heat transported by blood flow from the deeper to the more superficial areas. It is the latter factor which must account for variations in conductance. This effect is considerable. For a fall in skin temperature from 35 to 32 °C, conductance is cut in half (Winslow, Herrington, and Gagge, 1937). The values for conductance obtained by our procedure agree well with those derived by Burton and Bazett (1936).

Physiological Control of Metabolism

Under normal conditions, when the process of body-cooling reaches a certain point, shivering sets in and there is a tendency to other types of muscular movement (as when one slaps the chest to "keep warm"), which movement is accompanied by increased metabolism. This adaptation to cold by increase in metabolism has not been marked within the range of our experiments.

Physiological Control of Sweat Secretion

At high atmospheric temperatures, the chief adaptative resource is sweat secretion to increase evaporative heat loss; and the efficiency of this mechanism has been illustrated in Fig. 1. For sweat secretion, as for conductance, quantitative values may be obtained by the methods of partitional calorimetry. This value we have defined by the term *wetted area*, which is derived by the following procedure. The amount of moisture actually evaporated from the body is determined for varying air temperatures and air humidities (with standard minimal air movement) and converted into evaporative heat loss per unit area of skin. The vapor pressure of each atmosphere is known, and also the vapor pressure of the moisture present on the skin. Computation of the kilogram-calories per square meter per hour of evaporative heat loss per unit of vapor-pressure difference between skin moisture and air gives us a measure of the amount of moisture actually present on the skin surface. This has a maximum value of about 30 kilogram-calories per square meter per hour for each centimeter of Hg pressure difference. If sweat were secreted evenly over the entire body surface, this maximum would represent the point where the skin could be considered as theoretically covered completely and evenly with a very thin layer of water. Actually, of course, the observed value cited above

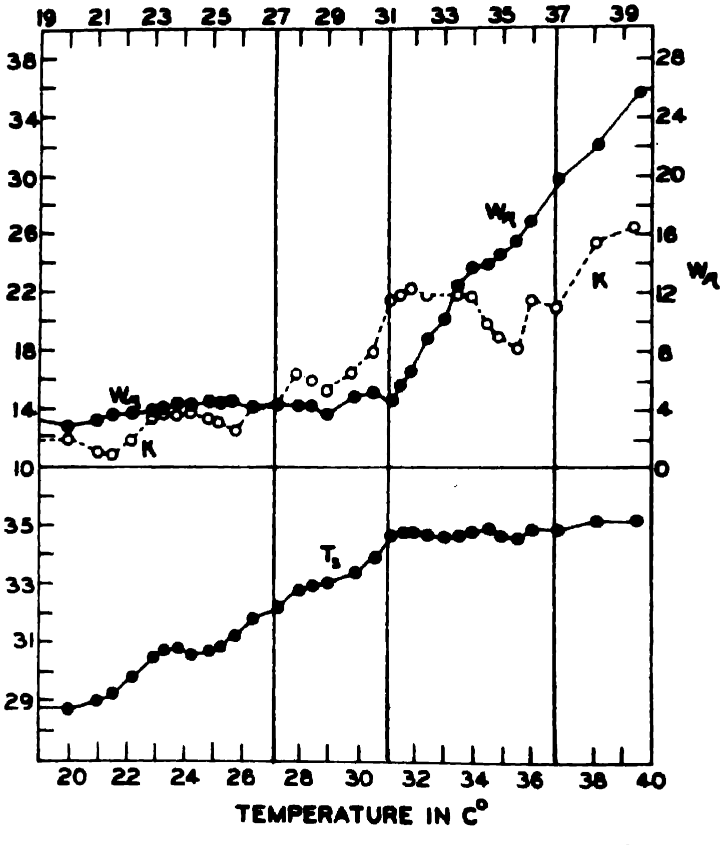


FIG. 4. Physiological responses to varying operative temperatures. W_t = wetted area, K = conductance, T_S = mean skin temperature. Nude subjects.

must represent a figure lower than this hypothetical one, since sweat is unevenly excreted. A minimum value of about 3 kilogram-calories is observed at low temperatures, representing the evaporation which occurs from the normal skin without active sweat secretion. Between this value and the maximum of 30 kilogram-calories, wetted area is a measure of the effective evaporative surface of the body (Gagge, 1937; Winslow, Herrington, and Gagge, 1937, 1938). The problem of evaporative rate has been approached by another method (vapor-tension measurements on the skin surface) by Buttner (1935, 1938).

Physiological Adaptation to Varying Environmental Calorie-Demand

The points at which these various physiological mechanisms operate is indicated in Fig. 4, as plotted against operative temperature (representative of the combined physical influences of air and wall temperatures) with moderate relative humidity and minimal air movement. The data are for nude subjects in the usual semi-reclining position.

It will be noted from Fig. 4 that, at operative temperatures below 27.5 °C, both conductance and wetted area show very slight changes. Between operative temperatures of 20 and 27°, conductance values increase only from 12 to 14 and wetted area values only from 3 to 4. At 27.5°, the peripheral blood vessels begin to dilate and conductance values rise rapidly, reaching a figure of 22 at 32°. Up to 31°, this mechanism is sufficient to keep the body in thermal equilibrium, although, as shown in the lower graph, there is a steady rise in skin temperature which shows values of 29° at 20° operative temperature, 32° at 27° operative temperature, and 35° at 32° operative temperature.

At 31 °C, a second mechanism comes into play, the active secretion of sweat, and wetted area rises sharply, from 5 at 31 ° to about 20 at 37 ° operative temperature, and to 30 at 40° operative temperature.

As soon as sweat secretion has set in at 32°, conductance and skin temperature increases cease, since evaporation is sufficient to maintain thermal equilibrium. This condition holds up to 37°. Here, sweat secretion is no longer adequate for its task and conductance begins to rise together with the wetted area and at about equal rate. It should be noted that most of these experiments were made with warm walls and cold air. As noted above, the physiological effect of a given operative temperature with warm walls and cold air is more cooling than when air and walls are at the same temperature. Therefore, for equal wall and air temtemperatures, the graphs would shift somewhat as compared with those of Fig. 4. The critical point of 31° seems, however, to be definite for a wide range of combinations of air and wall temperature.

Upper Limits of Evaporative Regulation

The process of evaporative regulation has, of course, an upper limit at the point where the sweat begins to run off without evaporating; and this point, as indicated above, corresponds to about 30 kilogram-calories of heat loss per square meter per hour per centimeter of Hg vapor pressure difference between skin and air. It is obviously possible to compute this upper limit for various combinations of air temperature and atmospheric relative humidity for a given metabolism and for the skin temperature associated with hot conditions. As seen in Fig. 4, skin temperature does not vary much in this region until the limit of evaporative regulation is

Upper Limits of Evaporative Regulation.

Environmental Temperature (°C)	Relative Humidity Nude Subject	Clothed Subject
52.7		0
50.0		5
45.0	1	18
42.5	13	26
40.0	29	38
37.5	47	51
35.0	70	69
32.5	100	89
31.0		100

exceeded (Gagge, Herrington, and Winslow, 1937; Winslow, Herrington, and Gagge, 1938). From such a computation, we obtain the figures on p. 519, for minimal air movement.

It may be noted that, at environmental temperatures which are above the optimum but below 35 °C, the nude body—as one would expect—can adapt to a higher relative humidity than the clothed human body. With still higher environmental temperatures, however, the presence of clothing is an advantage. Here, the skin is absorbing heat from the air by convection and the protective action of the clothing tends to limit this process. At the same time, the presence of clothing favors evaporative heat loss by increase of evaporative surface. This is why the wearing of clothing offers protection against the dry but intense heat of a desert climate.

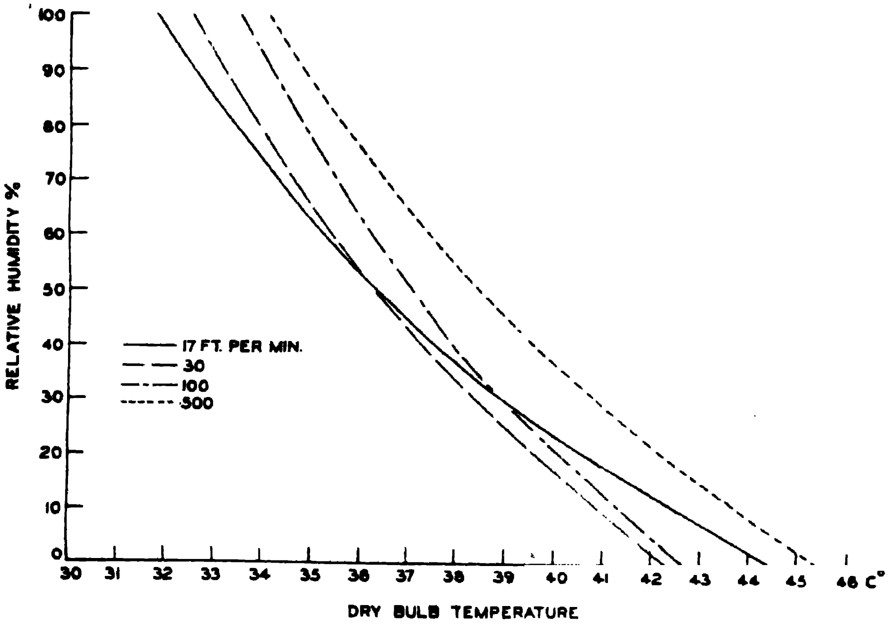


FIG. 5. Contour chart indicating upper limits (wetted area = 100%) of the zone of evaporative regulation for various air velocities. Nude subjects. (Gagge, Herrington and Winslow, 1937.)

The effect of air movement upon the upper limits of evaporative regulation has been theoretically evaluated by a similar procedure (Gagge, Herrington, and Winslow, 1937). It will be noted from Fig. 5 (for the nude body) that with high relative humidity and relatively low environmental temperatures, the cooling effect of increasing air movement exhibits a uniform relationship. With higher environmental temperatures and low humidities, however, where air is above skin temperature, the influence of increased air movement is to increase both convection heat *gain* and evaporative heat *loss*. The balance between these processes is such that an increase in air movement from 8.5 to 50 centimeters per second is actually unfavorable. Only when air velocity reaches 200-280 centimeters per second is a net increase in cooling effect produced.

It may be noted that the lowering of skin temperature associated with body-cooling and the active sweat secretion in the zone of evaporation regulation are both accompanied by marked sensations of discomfort (Winslow, Herrington, and Gagge, 1937; Gagge, Winslow, and Herrington, 1938), in spite of the fact that in the latter case, complete thermal balance is maintained.

Significance of the Results Reviewed Above

These are the principal results which have been obtained by recent applications of the procedures of partitional calorimetry. They are, perhaps, of some interest to the present symposium from the standpoint of temperature measurement, on account of the wide variety of methods for evaluation of temperature change involved. We have determined heat production in metabolism by the oxygen consumed in the process of slow tissue oxidation, and evaporative heat loss by weight of moisture loss. We have determined convection and radiation interchanges by applying theoretical reasoning and empirically-derived constants to temperature differentials between the skin and the air and walls, respectively, and storage processes by changes in skin and rectal temperature. The actual temperature changes involved in air and on skin and walls have been recorded by the responses to those temperatures of metal junctions. Air movement has been measured by temperature changes in a hot wire, and relative humidity by comparison of the response to temperature of mercury in a wet and a dry bulb.

It is only by such intensive studies of the quantitative influences of air temperature, wall temperature, air humidity, and air movement, of the physiological responses of the body to such influences, and of the limits beyond which its adaptive responses fail, that we can lay a basis for sound standards of practice in the control of our atmospheric environment.

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The Operating Characteristics of the Human Thermoregulatory Mechanism

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The extended use of thermoregulatory devices in science and industry has led to the development of a comprehensive theory of temperature control (Haigler, 1938; Bristol and Peters, 1938). The physiological mechanism by which the temperature of the human body is regulated may be profitably considered in the light of this physical theory. Two purposes may thus be served. The physiologist may see more clearly how much of the complexity he encounters is due to the interaction of familiar physical factors, and how much to new factors peculiarly physiological. The physicist may learn of new methods of control which are effective in a situation of greater complexity than those he usually encounters.

The regulation of the human body temperature depends upon three distinct mechanisms, each of which is the most important in a particular range of environmental temperature. Only one of these mechanisms will be considered in this paper, namely that operating in the range of 'comfortable' temperature where neither sweating nor increase of metabolism by shivering are called into play. The mechanism to be considered must carry nearly all the burden of control in our modern sheltered lives.

The first question of interest in the description of any thermoregulator concerns the nature of the 'controlled variable.' For the body the answer is not obvious. The temperature of the surface of the body is several degrees lower than the interior and differs greatly in different parts. Moreover, the lower temperatures exist as far as an inch below the surface (Bazett and McGlone, 1927) and quite 50 per cent of the whole body is within this distance of its surface. Which, then, of the many temperatures simultaneously existing in the body is the controlled temperature? The deep structures such as the heart, liver, and brain have normally very closely the same temperature, which is approximately that given by a thermometer placed well within the rectum. In health, moreover, this temperature, described as the 'deep body temperature,' remains between about 36.5° and 37.5 °C in a wide range of environmental temperature. In the same range of conditions skin temperature varies by as much as 10 °C. The 'deep body temperature' is then considered to be the 'controlled-variable' of the thermoregulator.

A physicist might expect to find the temperature-sensitive device of the mechanism located at some point which shared this controlled temperature, *i.e.*, the deep body temperature. There is indeed evidence, originally due to Barbour (1911) and recently made more conclusive by Magoun *et al.* (1938), that the region of the brain known as the 'heat-regulating center' in the hypothalamus is sensitive to the temperature of the blood passing through it. The main 'primary elements' of the mechanism, however, are undoubtedly the temperature receptors of the skin so well studied by Bazett and co-workers (1930) and by Hardy and Oppel (1937, 1938). Here then is a complex situation, where the temperature-sensitive elements actuate a mechanism which achieves the constancy of the temperature of a distant point. Moreover, the controlled temperature bears no constant relation to that of the receptors. If, like the expansion thermometers or thermocouples of the usual physical regulator, the temperature receptors of the skin responded only to the level of temperature, it would be difficult to conceive how the mechanism could operate. It is known, however, that their response depends also upon the rate of change of temperature and, in all probability, upon the thermal gradient in the skin (Bazett, 1927; Ebbecke, 1917). It is this peculiarity which makes possible the control of the temperature of a distant point.

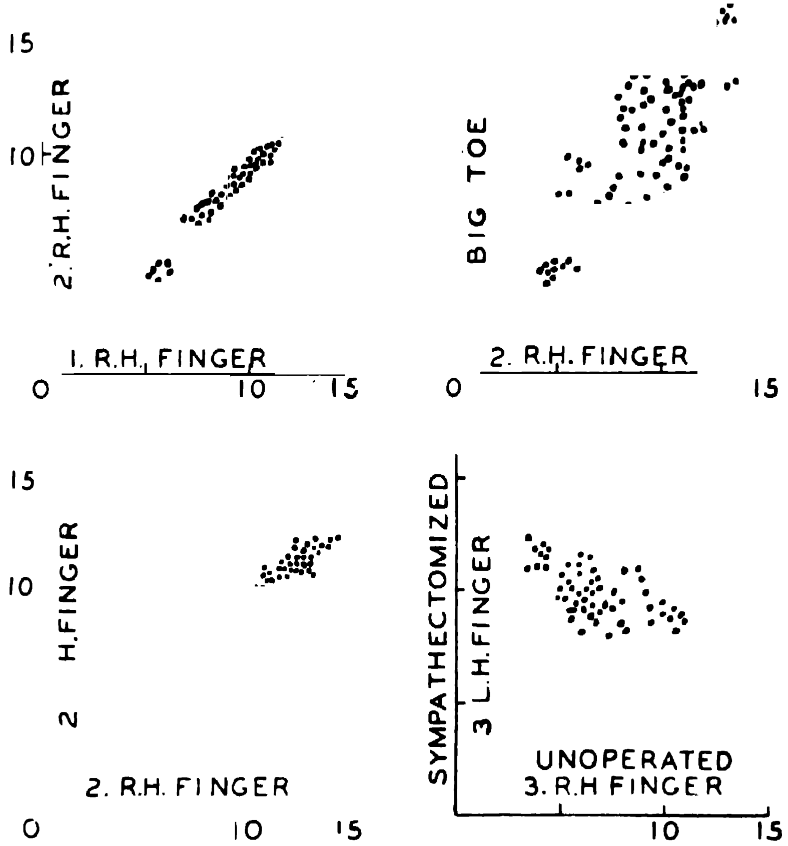

Fig. 1. Simultaneous values of the size of the volume pulsation with each heart beat of blood vessels in different parts of the body. In the last diagram pulsations in a limb deprived of its sympathetic nerves are compared with those in the opposite, unoperated limb. It shows that the sympathetic nervous system is responsible for the coördination of the changes. The units of the scales are mm of pulsation height on the photographic records.

The 'control agent' by means of which the central nervous system, responding to nervous impulses from the temperature receptors, achieves the regulation of body temperature is the adjustment of the blood flow of the peripheral tissues. In certain instances flow may be varied through a hundred-fold range (Burton, 1939) by the control of the sympathetic nervous system acting on the walls of the blood vessels.

In effect, the average thermal conductance of the peripheral tissues (or if you will, the insulation resistance) may be changed by a factor of five or six (Burton and Bazett, 1936; Winslow *et. al.*, 1937) in passing between full vasoconstriction and vasodilation of the blood vessels.

In the range of environmental temperatures under discussion the total heat production is not primarily involved in thermoregulation and its variations are controlled by other physiological factors, such as muscular exercise and food. Control of the deep body temperature is therefore dependent upon a regulation of the total heat loss. The rate of flow of heat from the center of the body to the surface may be expressed as the product of two factors: the equivalent thermal conductance, and the thermal gradient. A control of the conductance in accordance with the gradient would best regulate the total heat loss. It is thus a very attractive hypothesis that the receptors respond to thermal gradient in the skin rather than to level of skin temperature.

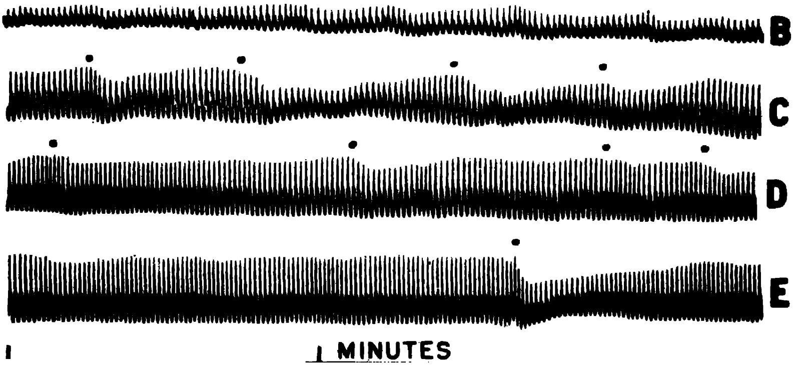

FIG. 2. Records of the volume pulsation of the finger vessels of a clothed subject in an environment of increasing temperature from *A* to *E*, which ranged from 22 to 30 °C.

Various types of control are recognized in the theory of thermoregulation, such as 'on-off' or two-position control, 'throttling' or 'proportional position control,' and so on. Recent experiments by Doctor Taylor and myself at the Johnson Foundation (Burton and Taylor, 1940) throw some light on the question of the type to which the human control mechanism may belong. The point of study was the fluctuation of blood flow in the fingers, which though so small a part of the whole vascular system, seems to be representative of coördinated fluctuations in the peripheral vessels in general. The sympathetic nervous system characteristically tends to carry simultaneous volleys of impulses to blood vessels all over the body surface and to the heart, and thus the changes in vasomotor tone in fingers, toes and other parts of the body are closely related (Fig. 1). There are undoubtedly local changes in blood flow in the skin which are not correlated with changes in other areas (Hertzmann, 1939). Because such changes are uncoördinated in different parts of the body, their effect on the average thermal conductivity of the peripheral tissues cannot play an important role in temperature regulation. The direction of change of the coördinated vasomotor adjustments which are controlled by the sympathetic nerves are, however, well indicated by the fluctuations seen in finger vessels.

In general it is found that the blood flow in the fingers is not maintained at any steady value, even though the environmental temperature conditions are kept constant. Blood flow is continually fluctuating widely between high and low values in a manner which is quite rhythmic. Continuous records of the pulsation of the finger volume with each heart beat show the nature of this fluctuation, for the degree of pulsation proves to be a reliable index of the blood flow under the conditions of these experiments. Fig. 2 shows a series typical of records taken in environmental temperatures which ranged from those in which the subject felt cold in (A) to uncomfortably warm in (E). At one end of the range of control the vessels are in maintained constriction, and blood flow remains minimal (A). Though little fluctuation in degree of pulsation is seen, there are periodic increases in heart rate (marked by dots over the record). These are an invariable accompaniment of widespread vasoconstrictions, for the cardiac accelerator nerves share in the activity of the sympathetic nervous system. Their presence in record (A), where rhythmic fluctuations in size of pulsation are not seen, indicates that superimposed on a background of vasomotor activity there is even here a rhythmic fluctuation. In warmer surroundings the dilations are more complete between successive vasoconstrictions. The period of recurrence of constrictions grows longer until finally the vessels are in almost continuous dilation (E) with only an occasional vasoconstriction. Both the amplitude of fluctuation and period of its rhythm are therefore modified by the thermal demand.

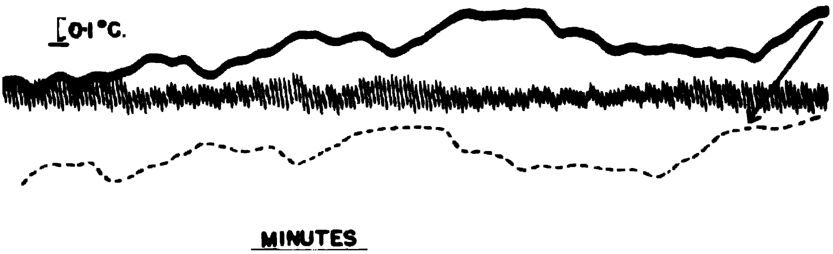

FIG. 3. Simultaneous records of volume pulsation of finger vessels and of the skin temperature of an adjacent finger. The broken curve is a tracing of the skin temperature record transposed along the time axis.

The picture is strongly suggestive of an 'on-off' type of control. If the analogy is true, there should be a correlated rhythm of fluctuation of temperature or gradient at the thermal receptors which is responsible for the maintenance of the rhythm of vasoconstrictions. Since the temperature of deeper structures is relatively constant, fluctuations in thermal gradient will be seen as changes of skin temperature. Accordingly, records of skin temperature have been made simultaneous with those of pulsation (Fig. 3). At first sight there is no relation between the fluctuations of the two; but if the record of skin temperature is transposed a distance equivalent to 20 or 30 seconds in time, a correlation becomes evident. Skin temperature is following the vasomotor changes with a time lag of about this amount. However, the correlation cannot be shown for any considerable length of record. It becomes evident that the amount of the thermal lag depends upon the level of the average blood flow at the time. Moreover, there are slow drifts of the average level of skin temperature according to the average flow of the preceding minutes, indicating that no single time lag is involved. We must consider also that the central nervous system integrates the impulses from receptors in the skin over all the body surface, and even if the vasomotor changes are simultaneous, the temperature changes, because of the differing thermal lags, will not be synchronous. In view of this integration and of the magnitude of the thermal lag at any given place, it is difficult to see how rhythmic changes in skin temperature can be initiating and maintaining the rhythm of vasomotor change.

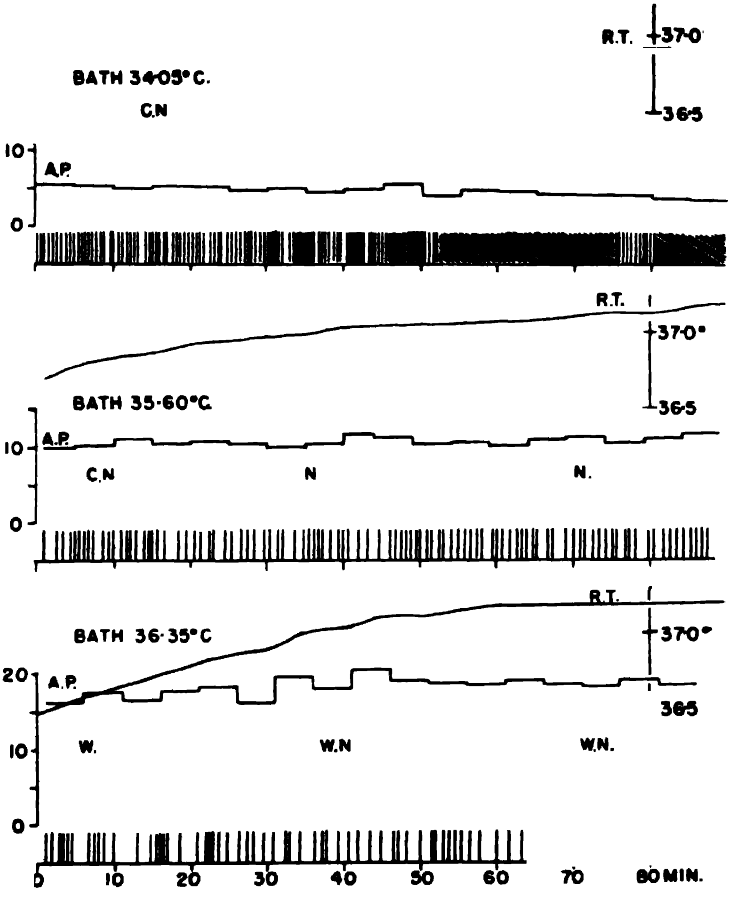

FIG. 4. Rectal temperature (R.T.), average size of volume pulsation (A.P.) of finger vessels, and diagrammatic representation of the occurrence of periodic vasoconstrictions in water baths kept constant at different temperatures. The letters *C* for "cool," *W* for "warm," *N* for "neutral" and their combinations refer to the reported sensations of the subject.

Fortunately, there are experiments which seem to settle the question conclusively. In a well-stirred water bath of constant temperature the changes in skin temperature may be almost completely prevented. Yet when experiments were made with subjects immersed to the neck in such baths, the rhythm of vasomotor fluctuation was still present and similar to that seen in an environment of air. The origin of the constrictions must be something other than the changes of skin temperature. The center in the brain may well have the intrinsic property of responding to a steady level of afferent stimulation, not by a steady but by an intermittent discharge, the rhythm of intermittence being modified by the intensity of the stimulation. Other centers, such as the respiratory center and the cardiac pacemaker, show this property. The operation of the thermoregulator is to be seen then, not in the occurrence itself of periodic constrictions, but in the modification of their rhythm in response to the thermal demand.

The bath experiments show that within the 'control range' between maintained vasoconstriction and vasodilation, the control is of the continuously variable type. In Fig. 4 the series of vertical lines represents successive vasoconstrictions in the vessels of the finger. (The cross-hatched areas represent periods of maintained vasoconstriction.) The slowing of the rhythm with increasing temperature of the bath is shown. Also plotted is the size of the pulsation averaged for five-minute intervals. This remains remarkably constant at a level which depends upon the bath temperature.

Each of the various types of control used in thermoregulators shows a characteristic temporary disturbance of the controlled temperature when the thermal demand is abruptly changed. The curve describing this disturbance, the 'response characteristic,' shows some unusual features in the case of the human mechanism. When the thermal demand is increased, instead of the temporary fall of the controlled temperature seen in most types of regulators, there is usually a temporary rise of the deep body temperature (Burton and Bazett, 1936). If the problem is treated theoretically by considering the body as consisting of cylinders of uniform thermal conductivity with a uniform heat production throughout, this paradoxical result is predicted when the thermal conductance is decreased in accordance with the increase of thermal demand. The unusual response characteristic is a consequence of the peculiar method of control by variation of the conductance.

Finally, like any physical regulator, the human thermoregulator is subject to 'load error' or 'droop,' *i.e.*, there is a shift in the final level of controlled temperature with a change in the thermal demand. In some recent experiments made by Doctor Bazett and his co-workers, subjects living in an air-conditioned room for several days maintained their body temperature at a level about 0.5 °C lower when the room was kept cold than when on the warm side of comfort. To minimize such 'load errors' thermoregulators are equipped with 'automatic reset' mechanisms. An example is that known as 'proportional-plus-floating control' analyzed by Mason and Philbrick (1940). These mechanisms operate usually by modifying the relation between the signals from the 'primary elements,' *i.e.*, the temperature-sensitive devices, and the resulting reaction of the 'control agent,' *i. e.*, the valve or heater. The modification depends automatically upon the deviation of the controlled temperature from the standard value.

The center in the brain is known to have a direct sensitivity to the level of blood temperature and may function as a 'reset mechanism' in a strictly analogous way. The excitability of the central cells may be peculiarly dependent on their temperature, so that the amount of efferent vasomotor discharge resulting from a given level of afferent stimulation from the receptors depends upon the deep body temperature. This is essentially the view suggested by Bazett (1927). Fluctuations in body temperature resulting from 'load errors' may thus be made much smaller than they would be if the human thermoregulatory mechanism employed the peripheral receptors alone.

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Heat Loss and Heat Production in Women Under Basal Conditions at Temperatures From 23 to 35 °C

J. D. HARDY, A. T. MILHORAT, E. F. DUBOIS

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Investigations of the relation of the factors of heat loss and heat production to changes in environmental conditions have been carried out in several laboratories on male subjects.[1,2,3] A really comprehensive study of these important relationships should include climatic adaptation, racial differences, and differences due to age and to sex. It has long been known that heat production in women is lower than in men, and other differences in the thermal responses of the sexes have been generally surmised. However, Oppel and Hardy,[4] in their study of temperature sensitivity, found no sex difference in the thresholds to heat and cold. It was the purpose of this study to measure the heat loss and heat production in young women at different environmental temperatures. Bodily activity and relative humidity in all experiments were low and varied little from time to time, so that the reaction of the subjects could be related to the single variable, environmental temperature. Menstruation was recognized as a factor which might affect the results and duplicate experiments at the same environmental temperature were made to evaluate this effect. No difference in response to the menstrual cycle was observed.

Method

All experiments were carried out in the calorimeter of the Russell Sage Institute of Pathology. The experimental procedure was essentially that used for the study of the male subjects and has been described in detail in previous publications.[5] As some additional steps were desirable in the present study, the routine of an experiment is briefly described. The subject arrived at the laboratory at about 8:30 A. M. in the postabsorptive state, having taken special care to do as little walking as possible. She sat quietly in normal indoor clothing in the calorimeter room, which had been set the day before at the experimental temperature. This period lasted for at least an hour and a half before the beginning of the experiment. The nurse was then called and assisted in making the first set of surface-temperature measurements. These readings were taken under the clothing just as the subject undressed. The nurse also weighed the subject, adjusted the rectal thermometer, and placed the subject in the calorimeter chamber. Following the sealing of the chamber, there was a preliminary period of usually an hour at the end of which the surface temperature was measured by the subject. The next period was basal during which the subject lay motionless for one hour. After the end of this period the surface temperature was again measured. The mean of these readings was taken to be the average skin temperature during the basal period. The experimental periods which followed were either basal or were utilized to study chills or exercise. At the end of the experiment the subject's blood pressure was measured.

All the subjects were highly intelligent and most of them were accustomed to laboratory procedures. Information concerning diet, etc., could be depended upon. The study was made on six healthy young women between the ages of 21 and 35, and included body types from the tall and slender to the short and heavy. The physical characteristics of the six female subjects together with those of the two male subjects previously studied are shown in Table 1, page 535. The general reactions of the six subjects under basal conditions to the changes in environmental temperature were essentially the same so that the group may be considered as a whole.

Results

Fig. 1 shows the observed changes.

(1) Rectal temperature showed considerable spread, but decreased slightly from the warm to the cold experiments. The points represent the average of measurements made at the beginning and end of the basal periods. It is evident that the internal temperature was slightly higher (0.15 °C) at calorimeter temperature 35 °C than at calorimeter temperature 23 °C.

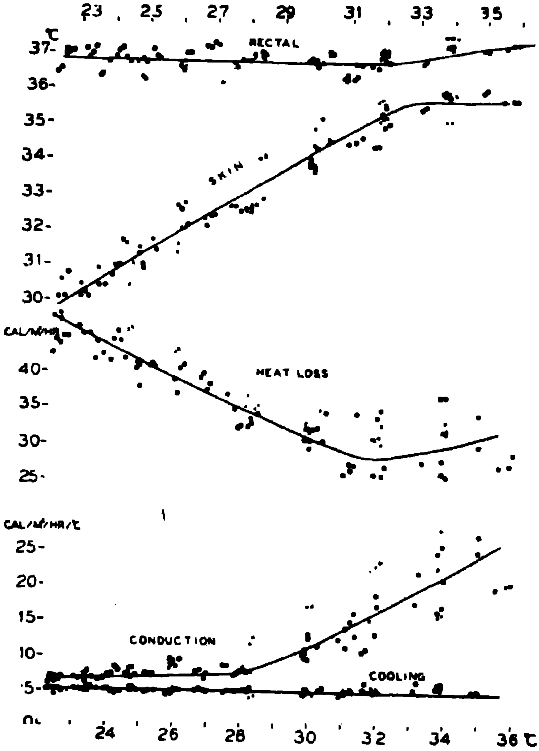

FIG. 1. Relationship of heat-loss factors to calorimeter temperature.

(2) The average skin temperature increased linearly with calorimeter temperature between 23 and 33 °C from its low average of 30 °C to its highest value of 36 °C. The skin temperature remained constant with further increase in calorimeter temperature and showed a tendency to fall with calorimeter temperatures above 35.5 °C.

(3) The heat loss also changed linearly with calorimeter temperatures, below 29 °C, and reached its lowest value of about 28 cals/m²/hr between 32 and 34 °C.

(4) The conductance of the peripheral tissues, which is measured by dividing the heat loss by the thermal head established between the internal organs and the skin, also changed linearly with calorimeter temperatures lower than 28.5 °C. Above this point there was a much greater increase in the conductance with temperature caused by dilatation of superficial vessels of the skin. From the figure it is evident that changes in peripheral conductance at high temperatures represented individual reactions. However there seemed to be two slopes to the conductance increases in the six subjects. Three followed one value (1.7 cals/m^2/hr/°C per degree rise in environmental temperature) and three a value of twice this amount.

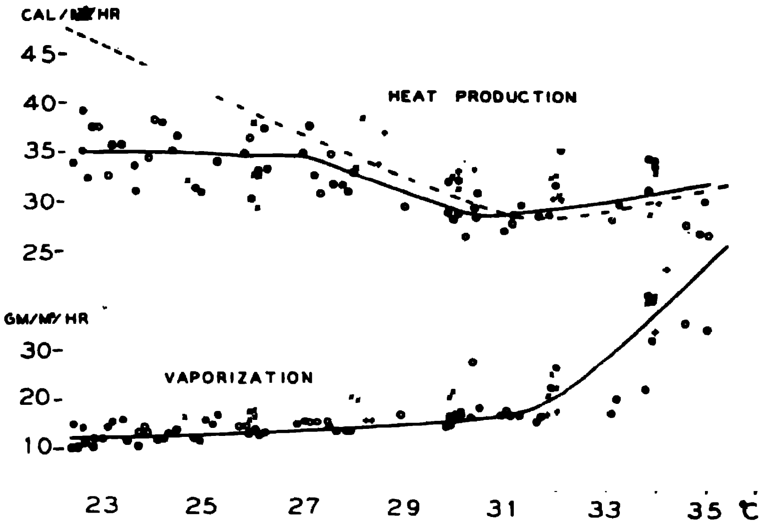

Fig. 2. Change in basal heat production and vaporization with calorimeter temperature.

(5) The rate of cooling, according to Newton's law, was constant throughout the experimental range, 5.3 cals/m^2/hr per degree difference in skin and calorimeter temperature.

The next figure shows the changes in heat production and amount of water vaporized from the skin and lungs.

The heat production in all but one subject showed a distinct fall in the range of calorimeter temperatures between 27 and 32 °C amounting to 5 to 6 cals/m^2/hr, or about 12 per cent. Below 27 °C the heat production was constant and above 32 °C it increased slowly. This change in the basal heat production is the first evidence of a chemical regulation of body temperature that we have been able to find in any of our studies, and appears to be a response to heat rather than cold.

The lower part of the figure shows that the amount of water vaporized from the body decreased linearly with calorimeter temperatures lower than 32 °C. Above this temperature there was considerable variation in sweating.

One of the interesting questions involved in this study is the comparative reactions of the men and women to changes in environmental temperature. The next figure shows a comparison between our two carefully studied men subjects and the women.

The internal temperature of all the men and women, so far as can be estimated, was the same. The women showed more variations in internal temperature than the men. The skin temperature of the women changed more, so that they were colder in the zone of body cooling and warmer in the zone of evaporative loss. The heat loss per unit area from the women was less than in the men although the loss per degree was the same for both. This means that the tissue conductance was lower for the women, as is shown at the bottom of the chart. The heat loss went much lower (6 to 7 cals/m^2/hr) in the women than the men. It is significant for the women that the heat loss and production were the same in these warmer experiments. The vaporization for men and women was much the same at low temperatures, but the men began to sweat at a lower temperature, and at higher temperatures sweat more than the women. The women had a much broader zone for natural regulation of temperature than the men by virtue of the ability to change their metabolic rate.

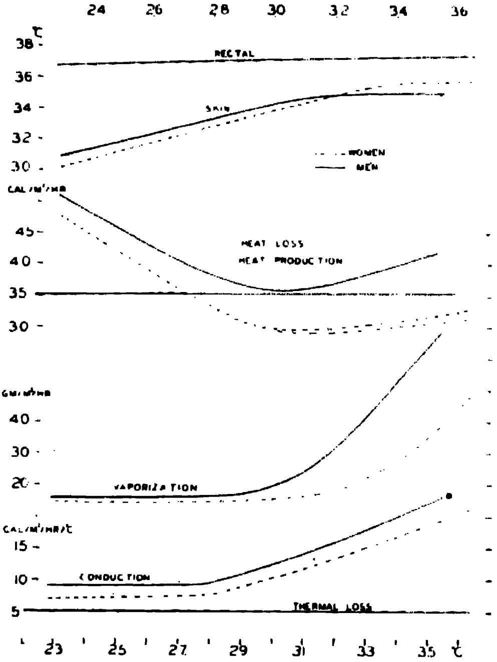

Fig. 3. Comparison of the responses of men and women subjects to calorimeter temperature.

In the next figure are shown the partitions of heat loss for the women and for the men and women compared. The significant differences in the sexes were the lower radiation losses for the women in the cold zone and the lower vaporization loss in the hot zone. The convection losses depended so much upon the amount of activity of the subject that the differences shown are not considered significant.

It would seem that there were significant differences in the responses of the men and women to change in environmental temperature in all the observed factors except the level of internal temperature and the thermal loss per degree from the skin. This suggests the importance of extending the experiments on environmental comfort conditions, which have been restricted to male subjects, to include a rather important half of the population.

Discussion

A. P. Gagge: The present paper is certainly a fundamental one and in the future will be a classic in a field that should have been explored long ago. There can be no doubt that we have here an excellent and thorough description of the thermal response of women to their environment. Comparison of these responses with those of men reveals, no doubt, where the probable differences lie, and confirms in a rational way what we all have suspected empirically from our experience with the other sex.

For the sake of clarity, I believe it would be advantageous to list the subjects and state their weight, height, surface area, etc., whether they are of the leptosomic or pyknic types. Although I have never seen it done before in calorimetric work, I believe there should be some statement in regard to normalcy in size of the subject. How do their weights compare with their heights on a basis of insurance company tables or some other nutritional authority? Is it high or low compared with their normal standard? Such a table would easily demonstrate that the subjects are a representative cross-section of the sex species, and it seems to me, would strengthen the argument of the paper considerably.

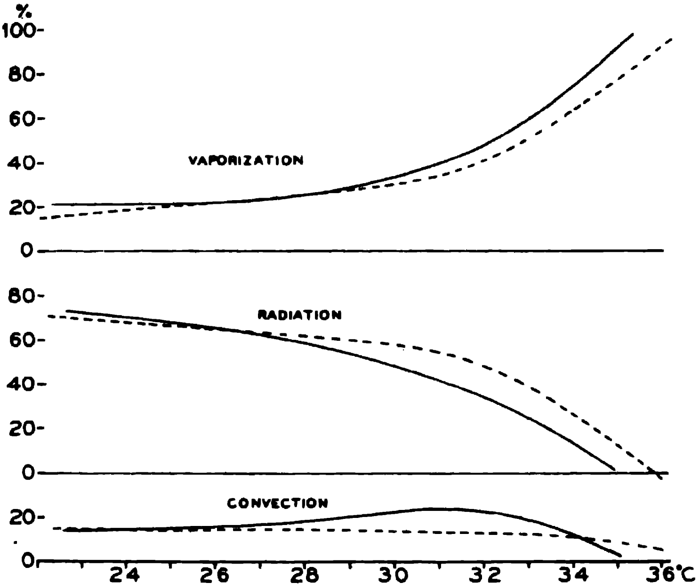

Fig. 4. Comparison of the heat loss by radiation, convection, and vaporization. Solid line, men subjects; dashed line, women subjects.

Carrying the same line of argument a step further, broader interest could be added to Figs. 1 and 2, if the subjects as listed were identified. Observation of the points in these figures shows that the subject with the cross (+) has a considerably different response from the subject with the open circle. Perhaps these variations could be explained by structural differences.

The weakness in the argument that there are definite differences between men and women lies in the fact that only two male subjects are compared with six women. In view of the variability of human physiology, it could be quite possible that the addition of data for two other male subjects could rule out the observed differences between men and women. The argument of the authors on this point would be strengthened, I believe, if they introduced a table showing that their male subjects were as comparably normal for their sex as their women subjects were. If the question of normalcy of subjects is indicated by a table listing the physical characteristics of all subjects, then the validity of these observed differences between the sexes may ride or fall on their own merits and not depend on the deductions of the authors.

There seems to be a slight ambiguity in the lowest curves at the bottom of Figs. 1 and 3. In Fig. 1, the *cooling constant* for each experiment is called "cooling;" in Fig. 3 the same item is labeled "thermal loss."

L. P. Herrington: These very interesting differences in the thermal responses of women as compared with men represent an important extension of information in this field. The results on conductance reflect, no doubt, the greater fat insulation of the female, and quite probably the higher level of vaporization in men is related to their greater heat load and a sweat center which is normally more exercised in the well-clad and active life of the male.

It would be very desirable to know how many of the subjects were at or near their menstrual period on the days when tests from 27 to 32° were made. On a chance basis it does not seem probable that the reduction in metabolism observed in this range could be due to a concentration of slightly pre- or post-menstrual measures. In view of the very great interest of this new and unexpected finding, however, it would be proper to exclude the possibility of measurements made during menstrual depression in future extensions of work on sex differences.

C.-E. A. Winslow: Dr. Hardy and his associates are to be congratulated on an admirable piece of pioneer work—the first quantitative analysis by modern exact methods of the difference in temperature response between men and women. All recent work has been with male subjects, and, as the authors say, it is highly important that we should know something about "a rather important half of the population." The lower conductance values for women are, of course, in accord with what is generally known as to their better-insulated peripheral tissues, but this is the first time this phenomenon has actually been mentioned. The more ready temperature-response of women as compared with men, at both ends of the temperature scale, is also highly significant; and the two phenomena taken together help to explain the frequently observed phenomenon of ready tolerance by women of temperatures that would be found uncomfortably cold by men, if they wore clothing of equally small protective value. On the other hand, the less ready sweat response shows why women generally object to high temperatures more than men.

It is very interesting to note the first demonstration in recent studies of what the authors describe as "chemical regulation." It might be questioned whether the term "regulation" is suitable, however, since the increase in metabolism in a warm environment is certainly not an active response.

Reply

Dr. Gagge's request for specific information concerning the subjects and their relation to the normal standards is a valid one. Therefore, we are including below a table of all the necessary data for the six female subjects and the two male subjects. We realize that the paucity of male subjects leaves us open to criticism in our comparisons of the sexes, but as our measurements are in good agreement with those made in New Haven at the Pierce Laboratory and those made by Newburgh in Ann Arbor, we felt that the information concerning male subjects was pretty well in hand. Also, we found nothing very unexpected in the behavior of our male subjects in any part of the temperature range investigated.

Dr. Gagge's question concerning the differences in the individual responses of the women subjects is explained in the table. The subject with the cross, Miss B, was quite different in her response to the warmer atmospheres. She was evidently not quite normal in the regulation of her peripheral blood flow.

Table 1. Individual Characteristics.

Subject	Symbol	Age	Ht. (cm)	Wt. (kg)	Surface area m²	Remarks
				Female		
G	●	35	175	64	1.77	Tall, well formed: laboratory technician, no physical abnormalities.
N	○	25	162	60	1.62	Artists' model: medium height and well formed; no abnormalities.
B	+	26	165	54	1.56	Actress: medium height, slightly underweight, well formed. Complained of inability to sweat and swelling of extremities in hot weather. Was observed to have abnormally large blood flow in warm experiments, with swelling of ankles.
W	×	25	165	55	1.58	Business woman: slightly underweight, receiving hormone therapy. Did not have a decreased basal metabolism in warm atmospheres.
S	◒	21	162	77	1.80	Laboratory technician: definitely overweight for her height; normal in other respects.
E	⊙	23	168	56	1.63	Laboratory technician: medium height and weight; no abnormalities.
				Male		
D		54	179	78	1.95	Physician: tall, well formed. No abnormalities.
H		33	168	67	1.77	Physicist: short, muscular. No abnormalities.

Dr. Herrington's question concerning menstruation: This was recognized by us as a factor which might affect our results. We made experiments at the same environmental temperature during the menstrual period and 14 days pre-menstrually. No differences in response to the menstrual cycle were observed. Analyses of the data show that only four experiments were made during menstruation in the whole series, and only two others within two days of either the beginning or the end of the menstrual period. The only relationship which we were able to discover between the spontaneous fall in metabolism and temperature was that the one subject who failed to show this effect was receiving hormone therapy for amenorrhea.

Dr. Winslow is quite correct in questioning our use of the term "regulation." Indeed, we do not know what is the basis of the fall in metabolism in the warm experiments. We can only say that the metabolism and the heat eliminated decrease in the same way.

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The Significance of the Average Temperature of the Skin

JAMES D. HARDY AND EUGENE F. DU BOIS

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It was in the early part of the century that G. N. Stewart[1] made the often-quoted remark that "There are several ways in which the skin temperature can be measured, but the chief difficulty is to know what to do with the data once we get them." The opinion of many who are working in this field today is almost the reverse of this statement. This is especially true since the interest in skin temperature has shifted from a study of the fingers and toes to investigations of the changes in the average temperature of the whole skin surface and its relation to heat loss. With this shift the physics and physiology of the regulation of heat loss from the body have become understandable, and many uncertain notions have been clarified. The greatest usefulness of the average skin temperature has been in interpreting the data in regard to regulation of body temperature through control of heat loss. On the basis of this information the environmental temperature range from 20 to 40 °C has been divided into three parts: first, the temperature zone in which the body loses heat at a rate greater than its normal basal metabolism; secondly, the zone of pure vasomotor regulation; and thirdly, the zone of combined vasomotor and evaporative regulation. Let us consider these zones and the significance of the *average* skin temperature in each.

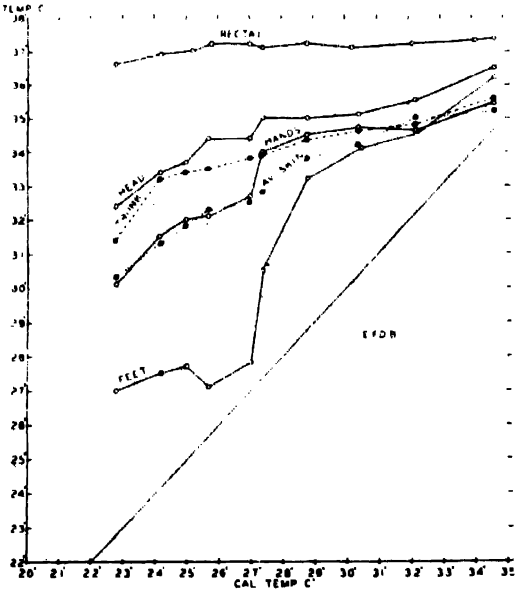

FIG. 1. Skin and rectal temperatures in normal man during basal experiments in the calorimeter at different environmental temperatures. The dotted line shows the average skin temperature.

The environment in which the nude, basal, male subject, lying motionless, loses heat more rapidly than he produces it is one cooler than 28 °C (83 °F). The first figure shows the changes in average skin temperature and of various parts of the body for a typical subject in a series of experiments, each at constant temperature, in the range from 23 to 35 °C. Each observation represents the average of two or more readings made after the subject had been exposed to the experimental environment for more than an hour and a half. In the range of body cooling, the only great change noticed in the separate parts of the body was the unusually low level of foot temperature below 29 °C. The other parts of the body changed temperature more uniformly with lowered room temperature, and the average skin temperature changed about .5 °C for each degree change in environment. This change in average skin temperature limits the heat loss in the temperature zone of body cooling. Fig. 2 shows how the sum of radiation plus convection changed with the environmental temperature. We may neglect vaporization for the moment because it was constant in this tempearture range. The obvious change was that, with lowered environmental temperature, the heat loss increased in proportion, and the average skin temperature fell in proportion. The question now arises, is this fall in average skin temperature of about 4 °C a physiologic response to the cold or a physical cooling resulting from lowered environmental temperature? The answer is in the curve, which shows that the conductance (written "conductivity" in figure) of the body was almost constant in this temperature range, or what is the same thing, the insulating power of the tissues was not increased by the fall in skin temperature. Conductance was computed from the following formula:

$$K = \frac{H}{A(T_r - T_s)}$$

Where K = conductance
H = heat loss
A = surface area of the body
T_r = internal body temperature
T_s = average surface temperature

Whatever vasomotor activity was present in this zone (and from Fig. 1, showing the fall in foot temperature, such activity must be assumed) it was not effective in control of heat loss. The fall in average skin temperature is thus the effect of physical cooling, and the body cannot control heat loss in this range of temperature. Here the balance between loss and production is effected by increased muscular activity.

What changes does one find in the average skin temperature when the body chills? The next figure shows this case. This typical experiment, in which the subject was naked and motionless, shows heat loss higher than heat production for the first hour. Skin and rectal temperatures fell until he shivered. The heat production rose 100 per cent with the chill, but the heat loss increased only 8 per cent, and this was because of the greater convection resulting from the body movement. In the next period the subject was quiet, having restored his body heat, and the higher skin temperature did little in the way of increasing heat loss. As a matter of fact, the subject was so quiet in the last period that the heat loss was reduced in spite of higher skin temperature. There is an interesting consideration here; that is, raising the average skin temperature in a given environment has relatively little effect in increasing heat loss because one is depending on cooling by radiation and convection. Under our experimental conditions the increase in heat loss caused by a rise of 1 °C in the average skin temperature was only 5.3 cals/hr/cm². The body is often called upon to eliminate four hundred calories per hour, so the ten to fifty calories that can be lost by increased radiation and convection do not nearly meet the demand.

The next figure shows the basal experiments for the whole experimental range, but we shall consider first the zone of pure vasomotor regulation represented by the small temperature range from 28.5 to 30.5 °C. Here heat loss and production were nearly equal. In this zone all parts of the skin surface were at about the same temperature and changed together. One finds neither shivering nor sweating in this zone. The conductance (conductivity) of the tissues increased and decreased with the temperature of the environment, and we see evidence of effective control of heat loss by automatic changing of the average surface temperature. The total amount of this change was small, between 0.7 and 0.8 °C. That is, when the subject lay nude and motionless, the average skin temperature was shifted to meet the demands of the environment by decreasing blood flow and cooling as the environmental temperature fell, and by reverse action as the surrounding temperature rose. In these special circumstances a rise in average skin temperature indicated increase in blood circulation in the skin, and vice versa.

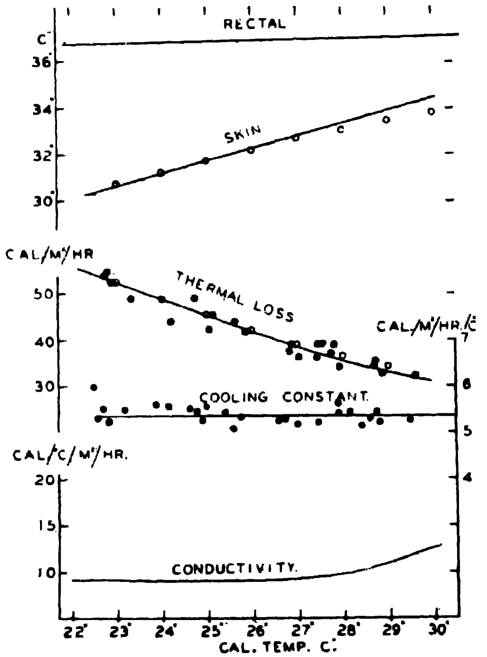

FIG. 2. Relationship between thermal properties of the body and calorimeter temperature. Solid lines represent average values from measurements on two subjects; solid dots, observed values; open circles, calculated values from Newton's Law.

The zone of evaporative regulation begins at about 30.5 °C with sweating over the body surface and increased skin circulation. The average skin temperature changed very little until environmental temperatures above 36 °C were reached, and then it began to fall. In this zone and in the zone of vasomotor control, the slightest exercise invariably caused a fall in average skin temperature. This

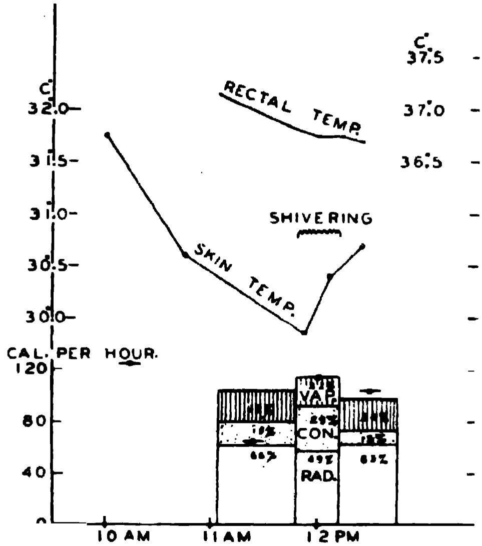

FIG. 3. Changes in heat production and heat loss before, during, and after a spontaneous chill in a man lying nude in the calorimeter. Temperature, 23 °C.

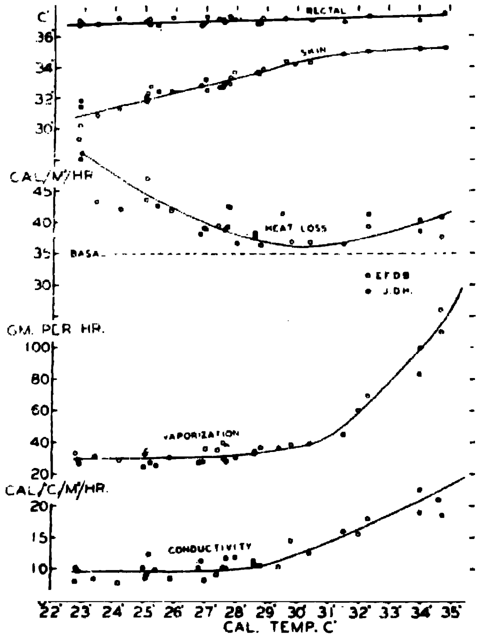

FIG. 4. Changes in rectal and skin temperature, heat production, heat elimination, vaporization, and conductance (conductivity) of two normal men during basal periods with increasing calorimeter temperatures.

decreased skin temperature was, of course, the result of sweating. Thus, the skin temperature fell with increasing skin circulation. Burton [2] has shown that the skin temperature of the leg, trunk, and arms rises slightly at the start of exercise and later falls because of sweating. This corresponds to passing through the phase of pure vasomotor regulation into the phase of evaporative loss. This is well demonstrated by the chart of exercise which has been used once before at this symposium, showing that, as the demand for heat loss increased, the average skin temperature fell, although there was reddening of the subject's skin from maximal vasodilitation. In most conditions it would seem that an *increased* skin circulation is accompanied by a *fall* in average skin temperature, because as soon as any appreciable vasodilitation occurs sweating begins. The surface temperature of the hands and feet, however, almost invariably is raised under these circumstances. The significance of the average temperature of the surface of the body is now clearly seen to be that of fixing the internal thermal gradients of the body in the zones of physiologic regulation and setting the limits to heat loss in the zone of body cooling.

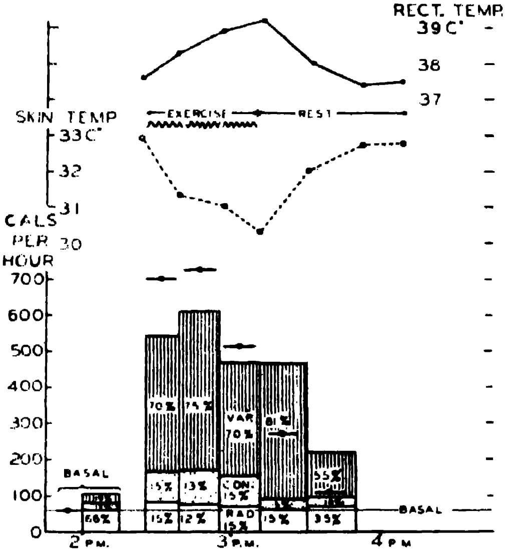

FIG. 5. Diagram showing the effect of violent exercise. Subject played three games of squash-racquets. The rectal temperature rose sharply to fever levels, the skin temperature fell. The round dots with horizontal lines through them show the estimated heat production, and the columns the estimated heat loss.

In summary, it may be said that changes in surface temperature have an important effect on radiation when a man is quiet in a cool room. With activity the total loss through radiation may remain the same but its percentage diminishes. Skin temperature has a similar relation to convection, but movement of air is usually much more important. Vaporization is the great emergency channel of heat loss and causes a fall in average skin temperature. The significance of the average skin temperature as regards evaporation in cool environments lies in the fact that the vaporization of moisture from the skin surface is affected but little by the relative humidity. This is due to the fact that the average skin temperature is several degrees higher than that of the environment. Thus the vapor pressure of moisture at skin temperature is greater than that of saturated air at room temperature, and evaporation will take place almost as readily in saturated air as in relatively dry air. Finally, in consideration of the surface temperature in heat loss the total area of the skin is of importance and attention should not be focussed alone on fingers and toes, which are only a small part of the whole surface.

Discussion

William Bierman: We are much indebted to Drs. Hardy and Du Bois for their clarification of the manner in which heat is lost from the human body in environments of varying temperatures. Their emphasis upon the need for observing particularly the *average* skin surface temperature rather than the more widely oscillating ones of the extremities serves to show that in a cold, comfortable, and hot environment the body depends on three different technics in the effort to maintain its thermal homeostasis.

In the general problem of heat physiology, the point of view here described is unquestionably the most logical one. From the angle of particular interest to the clinician who utilizes the body's thermal fluctuations as a diagnostic aid in the evaluation of peripheral vascular disease and of differing procedures in its treatment, the responses of the skin surface and internal structures of the extremities are of more practical value. Even here, however, the elucidation of the general problem of body response to a changing environmental temperature will be of great assistance, and for it the clinician is much indebted to Drs. Hardy and Du Bois.

Bayard T. Horton, M.D., Division of Medicine, The Mayo Clinic, Rochester, Minnesota: Dr. Hardy and Dr. Du Bois have presented an interesting and valuable piece of investigative work, which throws additional light on the problem of exchanges of heat between the body and its environment. This particular study of determining the average skin temperature is of more vital interest to the physiologist and the physicist than to the clinician. During the past decade there has been a tremendous awakening of interest in the subject of peripheral vascular disease. Clinicians have become interested more and more in surface temperature, particularly of the extremities. I venture to say, however, that the clinician seldom has occasion to utilize the average skin temperature which has been worked out so carefully by these investigators. In the study of peripheral vascular disease, the clinician is interested primarily in the blood supply to the extremities and digits. He uses surface temperature as an index of blood supply to the skin. When an occlusive arterial disease is present, the preservation of the extremity depends on an adequate blood flow to the diseased part. Gangrene, when it develops, begins in the skin and not in the deeper structures, and it invariably starts in the area of the skin which has the poorest blood supply. The significance of skin temperature of the digits thus becomes obvious.

Stewart's statement that "there are several ways in which the skin temperature can be measured, but the chief difficulty is to know what to do with the data once we get them" was appropriate at the time it was written, but hardly seems so now.

For a number of years Drs. Sheard, Roth and I have been interested in the determination of skin temperature of the extremities. For the past three and a half years we have felt that we could apply these data to clinical problems. We have studied the surface temperatures of the extremities of numerous normal subjects as well as those of patients with peripheral vascular disease under controlled environmental conditions with the subjects in a basal state. Such a study has served materially to clarify many previous vague conceptions regarding the significance of changes in skin temperature and resulting blood flow in the extremities. These investigations have been of great importance not only from a diagnostic but also from a prognostic standpoint. Studies of surface temperature of the extremities aid in distinguishing between occlusive arterial disease and vasospastic disturbances. All our subjects with peripheral vascular disease are studied in this manner. Furthermore, data on the skin temperatures of the extremities are essential in selecting certain subjects for sympathectomy, and in eliminating those who are not suitable for this surgical procedure.

Reply

Dr. E. F. Du Bois: I am glad that Dr. Horton and Dr. Bierman have emphasized the clinical importance of the hands and feet. The study of temperature fluctuation over the rest of the surface is comparatively recent and we do not yet know its significance in our understanding of disease. From the standpoint of heat loss it is much more important than the relatively small areas of the hands and feet.

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Standard Operative Temperature, a Single Measure of the Combined Effect of Radiant Temperature, of Ambient Air Temperature and of Air Movement on the Human Body

A. P. GAGGE

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Introduction

In the preceding papers of the present symposium we have heard a very complete description of the temperature response of the body to its environment, what the basic underlying physiological processes are, and how, within certain environmental temperature limits, all combine in a resultant internal body temperature of 37 °C for the normal healthy human being. This homothermic property of our human body, coupled with two facts, first that we are pretty much of a blackbody to radiation, and secondly, that we are aqueous by nature, makes it necessary to describe our environment in more complicated terms than a simple ambient air temperature. Experience teaches us that, in addition, we must consider humidity, radiant temperature of our surroundings (in colloquial terms, wall temperature), and last but not least, air movement. The purpose of the present paper is to establish a temperature scale which, as a single value, describes the combined thermal as well as kinetic properties of our environment. For the present changes in humidity will not be considered in our discussion, nor does it seem necessary to be included, as it plays no part in the thermal exchange between man and his environment. Its only effect is on the efficiency of the evaporative regulative process—all of which is on the physiological side of the picture and not on the environmental in the strict thermal sense. Therefore, in the present paper the three factors, ambient air temperature, mean radiant wall temperature, and air movement, will be reduced to a single temperature, that satisfies Newton's Law of Cooling with a cooling constant comparable in magnitude to the value 5.3 Calories per square meter per hour per degree centigrade reported earlier by Hardy and Dubois in this symposium.

Standard Operative Temperature

For the present let us suppose that air movement is held constant; then loss by radiation and convection for the human body may be expressed as

$$R + C = K\,(T_S^4 - T_W^4) + K_C\,(T_S - T_A), \tag{1}$$

where

T_S = surface temperature of body,
T_W = mean radiant wall temperature,
T_A = ambient air temperature.

As a first approximation (1) may be written

$$R + C = K_R\,(T_S - T_W) + K_C\,(T_S - T_A). \tag{2}$$

But Newton's Cooling Law states

$$R + C = K_0\,(T_S - T_0), \tag{3}$$

where

T_0 is the operative temperature of the environment,

and

K_0 the associated cooling constant.

Comparing (2) and (3), we see that

$$T_0 = \frac{K_R T_W + K_C T_A}{K_R + K_C}, \text{ and } K_0 = K_R + K_C. \qquad (4)$$

That is, when air movement is constant, T_0 is effectively the average between T_W and T_A weighted according to the relative effectiveness of T_W and T_A. Any change in the relation of K_R to K_C automatically changes the value of T_0, *e.g.*, for a cold environment where T_W is greater than T_A, a fat man would be exposed to a lower operative temperature than a thin man, since his radiative area relative to convective area is less. On the other hand, if T_W were less than T_A, his shape factor would be an advantage.

It has been shown experimentally (Winslow, Gagge, and Herrington, 1939) that the loss by convection is proportional to the square root of the air movement,

$$C = k_C \sqrt{V}(T_S - T_A). \qquad (5)$$

We know from experience that the effect of air movement is essentially to make the ambient air cooler than it really is. Let us ask, at what temperature, T_A', with a standard air movement, V_0, does one lose the same heat by convection as at the observed temperature, T_A, and air movement, V. From

$$k_C \sqrt{V}(T_S - T_A) = k_C \sqrt{V_0}(T_S - T_A')$$

we see that

$$T_A' = \left(\sqrt{V/V_0}\right) T_A - \left(\sqrt{V/V_0} - 1\right) T_S. \qquad (6)$$

By (6) we may, therefore, describe any combination of V and T_A in terms of an equivalent air temperature (T_A') at standard air movement, V_0. The presence of T_S in (6) is necessary as T_A', by definition, has no meaning except for objects whose surface temperature is other than air temperature.

If we assume now that (4) is valid for standard air movement, V_0, substituting (6) in (4), we have

$$\text{Standard Operative Temperature} = \frac{K_R}{K_0}[T_W] + \frac{K_C}{K_0}\left[\left(\sqrt{V/V_0}\right) T_A - \left(\sqrt{V/V_0} - 1\right) T_S\right], \qquad (7)$$

where now

$$K_C = k_C \sqrt{V_0}.$$

Therefore, from (7), the temperature resulting from the physical combination of T_W, T_A, and V describes an imaginary environment of equal wall and air at standard air movement, V_0, in which the human body, if placed with the observed surface temperature, T_S, would lose the same amount of heat by radiation and convection as in the original environment. Further, Standard Operative Temperature satisfies Newton's Law with a cooling constant, K_0, which is the sum of the radiation and convection constants at the chosen standard air movement. In conclusion, therefore, from (7) we see that the Standard Operative Temperature of any environment to any animal body is a function not only of T_A, T_W, and V, but of its position (indicated in relative value of K_R to K_C) and of the actual temperature of its exposed surface, T_S. Finally, it may be noted, for a clothed subject,

T_S represents the mean temperature of the clothed surface and exposed skin surfaces, while for a nude subject, T_S is the mean skin temperature itself.

Experimental Results

The intended purpose of a temperature scale such as Standard Operative Temperature is to order data taken under any combination of T_A, T_W, and V, such that the various well-known physiological properties of the human body appear in their customary order. To be a successful temperature scale, Standard Operative Temperature should "normalize" data from partitional experiments into a pattern capable of ready analysis along lines already familiar (Winslow, C.-E. A. This symposium).

For this purpose, in Table 1, are shown the general experimental data for various air temperatures ranging from 35 to 22 °C, and various air movements ranging from 7.6 to 264 cm/sec. For purposes of our experiment the wall temperature has been made equal to the air temperature, and we have particularly emphasized changes in air movement. As before, for experiments in the Pierce Partitional Calorimetry, the subjects were at rest in a semi-reclining position. Variations in air movement were made by adjustment of six fans directed at the subject. Air movement measurements represent an average of air movement readings over the experimental chair without the presence of the subject. For details of the various experimental procedures used, the reader is referred to our previous publications on Calorimetry (Winslow, Herrington, and Gagge, 1936, 1937). Previous experimental work has shown (Gagge, Winslow, and Herrington, 1938) that for nude subjects the value of $\frac{K_R}{K_R + K_C}$ and $\frac{K_C}{K_R + K_C}$ are 48 and 52 per cent, respectively, at an air movement of 7.6 cm/sec (15 feet per minute). By choosing 7.6 cm/sec, therefore, as our standard air movement, the Standard Operative Temper-

Table 1. Data for Nude Subjects.*

Condition	T_A °C	RH %	V cm/sec	T_R °C	T_H °C	T_U °C	T_T °C	T_L °C	Mean T_S °C	S.O.T. °C	M	E	$R+C$	S
												Kg-Cal/sq m/hr		
1	35.3	50	7.6	37.56	36.5	36.1	35.8	35.8	35.9	35.3	52	−49	−4	1
2	35.1	50	51	37.22	35.5	35.4	35.2	34.9	35.1	35.0	46	−44	−1	−1
3	35.3	49	132	37.00	35.5	35.4	35.1	34.9	35.1	35.7	48	−42	4	−10
4	35.3	49	264	37.17	35.4	35.3	35.2	35.0	35.2	35.8	49	−44	4	−9
5	33.1	51	7.6	37.11	36.0	35.9	35.5	35.2	35.5	33.1	47	−30	−17	0
6	33.4	49	51	37.06	35.7	35.6	35.4	35.3	35.5	32.2	48	−21	−23	−4
7	33.7	49	132	36.94	35.3	35.4	35.2	35.2	35.3	31.2	50	−16	−29	−5
8	33.9	50	264	36.94	35.1	35.3	35.2	35.1	35.2	30.8	45	−16	−30	1
9	31.3	52	7.6	37.06	35.2	35.3	34.9	34.8	34.9	31.3	46	−21	−25	0
10	31.4	47	51	36.83	34.2	33.8	33.8	33.7	33.8	29.5	46	−16	−30	0
11	31.4	50	132	36.94	33.7	32.8	33.1	32.8	33.0	28.8	47	−13	−30	4
12	31.4	50	264	37.00	33.4	32.8	33.3	32.8	33.1	27.3	50	−14	−40	6
13	27.3	49	7.6	36.89	34.5	34.4	34.1	33.7	34.1	27.3	43	−13	−48	18
14	27.6	50	51	36.89	33.1	31.8	32.4	31.6	32.1	23.7	50	−12	−59	21
15	27.7	46	132	36.89	32.4	30.8	31.8	30.8	31.3	21.7	49	−12	−68	31
17	22.4	51	7.6	36.94	33.6	33.0	32.7	31.8	32.6	22.4	52	−12	−72	32
18	22.3	50	51	36.94	31.5	30.1	32.1	30.8	31.2	16.1	54	−11	−75	32

* T_A—ambient air temperature; RH—relative humidity; V—air movement; T_R—rectal temperature; T_H—of head; T_U—of upper extremities; T_T—of trunk; T_L—of lower extremities; T_S—mean skin temperature weighted (head, 7; upper extremities, 21; trunk, 31, and lower extremities, 41); S.O.T.—standard operative temperature calculated from (7); M—metabolism; E—evaporation; $R+C$—radiation plus convection; S—storage.

ature has been calculated for each of the 17 conditions. The column headed storage, S, is found by difference from the usual heat-loss equation,

$$M + S - E = R + C. \tag{8}$$

The physiological mechanism most sensitive to thermal changes in the environment is our sensible perspiration mechanism, or, more subtly said, evaporative regulation. The first test of Standard Operative Temperature should be to show how this particular factor is normalized. This is done in Fig. 1. In the top half is shown E plotted against the ambient air temperature, but classifying the various points according to their proper degree of air movement. In the bottom half is presented E now plotted against Standard Operative Temperature, but still the air movement classification is retained. One sees immediately that excellent

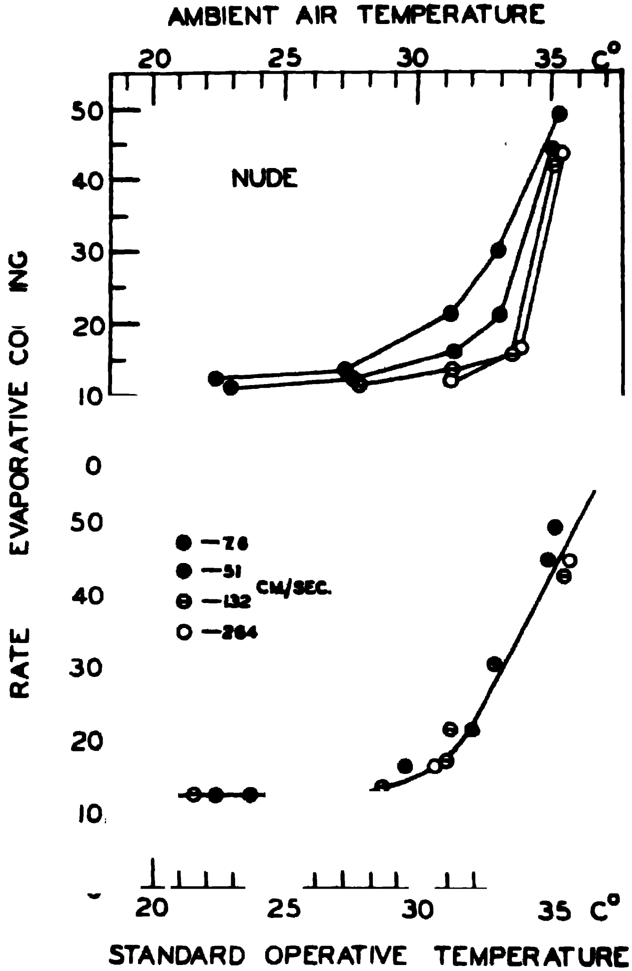

Fig. 1. Relation of evaporative cooling to ambient air temperature and standard operative temperature for various air movements.

normalization has been attained. The onset of evaporative regulation now appears at the customary temperature of 31 °C. It is interesting to note the convergence of the evaporation curves at an ambient air temperature of 35 °C. At 35 °C it appears that the rate of total evaporation does not change with air movement. However, as air movement obviously increases the efficiency of evaporation, it follows that with the same increase at 35 °C the extent of sweat secretion must considerably decrease.

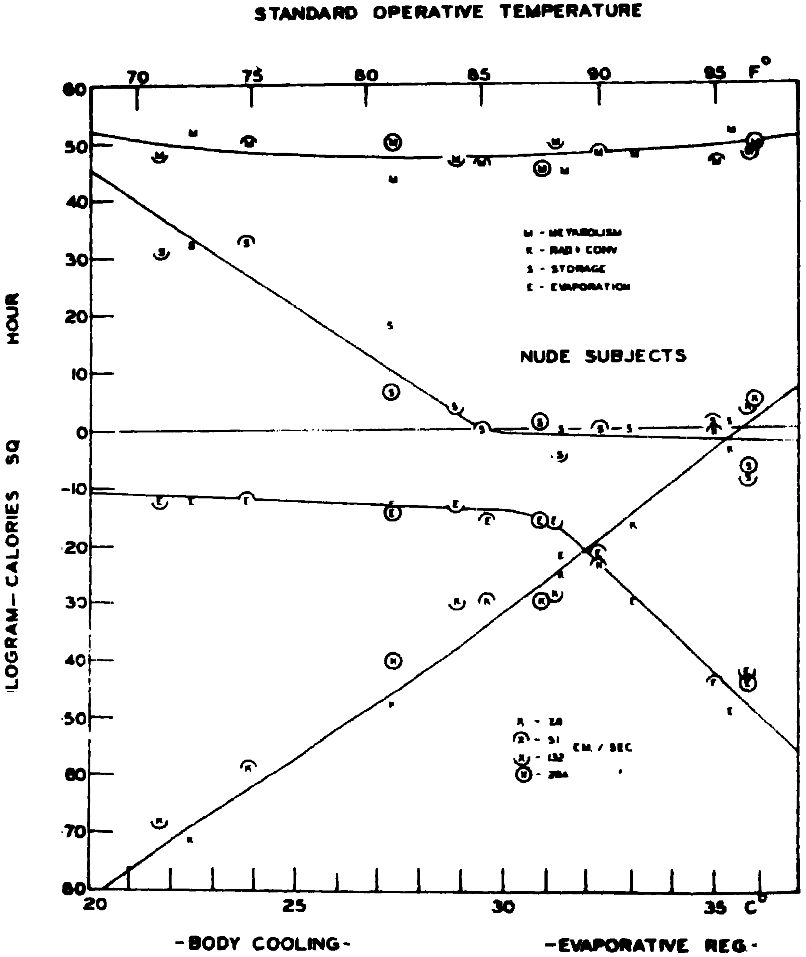

FIG. 2. Chart indicating how metabolism, storage, evaporation, and radiation plus convection are normalized by standard operative temperature for conditions where air movement varies from 7.6 cm/second to 64 cm/second.

In Fig. 2, the four general avenues of thermal interchange, namely, *M*, *E*, *S*, and *R* + *C* are plotted against Standard Operative Temperature. Again we see a successful normalization of the data. We see that the Zone of Body Cooling extends to temperatures below 29 °C, while as before the Zone of Evaporative Regulation extends above 31 °. Between 29 ° and 31 ° is the Zone of Vasomotor Control.

These limits agree very well with those previously reported for radiation data (Winslow, Herrington, and Gagge, 1937) and for the Russell Sage Calorimeter (Hardy and Du Bois, 1937).

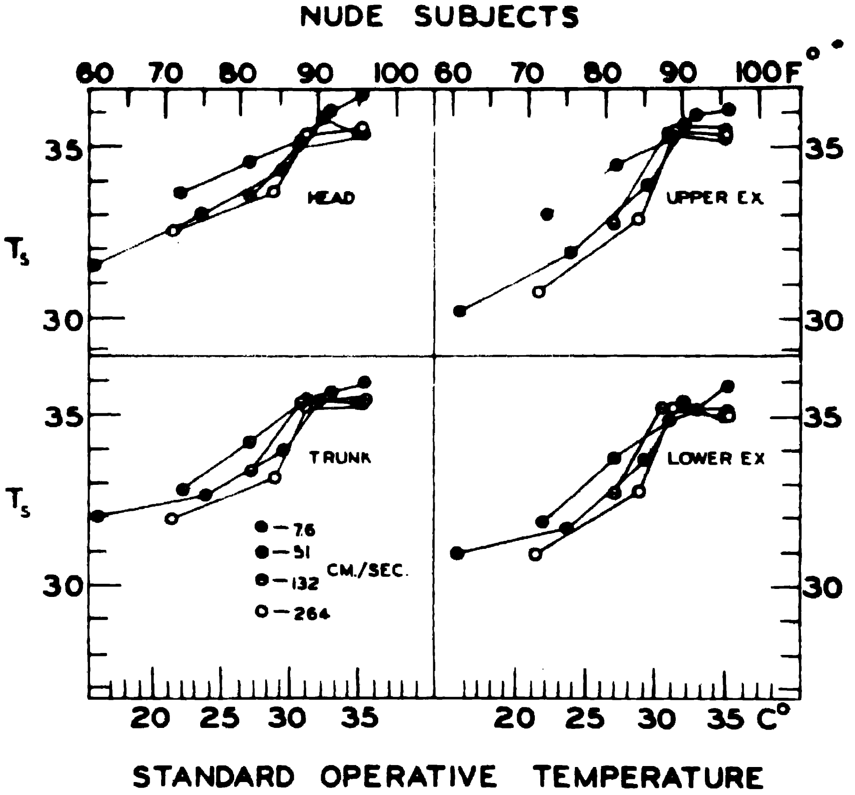

FIG. 3. Relation of segmental skin temperatures to standard operative temperature for various air movements.

In Fig. 3 are presented four curves showing how the temperatures of the head, upper extremities, trunk and lower extremities all vary with Standard Operative Temperature. As reported previously for data where radiation was the major variable, the skin temperature tends to level off above 31 °C. Below 31°, however, for the same operative temperature, increasing air movement tends to lower skin temperature. This apparently indicates a vasoconstrictive effect of air movement as a kinetic factor on the skin surface.

In conclusion it may be mentioned that similar normalization of data may be attained for clothed subjects. Results leading to practically identical conclusions will be presented elsewhere and need not be repeated in this paper.

Discussion

The usefulness of Standard Operative Temperautre for higher air movements as a means of normalizing data to a temperature scale already associated with various physiological processes is apparent from the foregoing experimental results.

This particular section is directed to workers who use conditioned chambers where the air movement is caused by whatever normal ventilation is necessary for the maintenance of the chosen temperatures, and also to those who seek a standard temperature scale for a comparison of their work with other workers in the same field.

In general practice the air movements encountered in ordinarily occupied rooms vary up to 51 cm/second (100 feet per minute), with a usual average in the range 10-15 cm/second (20-30 feet per minute). In well-designed test spaces where the subject has reasonable protection against the ventilating equipment, the range of air movement may very easily vary between 3.8-15 cm/second (7-30 feet per minute) depending on the position of the subject, arrangement of apparatus, etc. The chosen standard air movement for our experiments, 7.6 cm/second (15 feet per minute), is believed to be a practical one, as it actually represents relatively still air and at the same time allows sufficient air movement necessary for the maintenance of the desired experimental conditions. The purpose of the present section is to show how Standard Operative Temperature varies for velocities above and below the standard air movement, in particular for the range from 3.8 to 15.2 cm/second (7.5 to 30 feet per minute)—a range likely in normal ventilation practice.

In Table 2 the values of Standard Operative Temperature for various combinations of ambient air and skin temperature and air movements are tabulated. As would be expected from (7), in general Standard Operative Temperature in relation to ambient air temperature increases for air movements below the standard and decreases above the standard. As T_S drops, the Standard Operative Temperature increases for air movements above normal, and decreases for air movements below normal. Further, as the difference between skin and air decreases the range of variability of Standard Operative Temperature with air movement 3.8-15 cm/second (7.5-30 feet per minute) decreases. In Table 3 values derived from Table 2 have been entered. For a given T_S-T_A difference it is apparent that each degree variation in T_0 represents a variation in heat loss of 7.0 Kg-Cal/sq m/hr/°C—our Newton Cooling Constant. The third column of the table evaluates the degree of variation in terms of Kg-Cal/sq m/hr. The importance of the magnitude of this variation is seen when we compare these Calorie values with the average expected metabolism, 45 Kg-Cal/sq m/hr. These percentages are indicated in the fourth column. Table 3 shows the importance of not depending on the difference between skin and air temperature alone as a measure of heat loss. Often discrepancies in

Table 2. Variation of Standard Operative Temperature with Skin Temperature at Low Air Movements.

Ambient air temperature (°C)	Skin temperature (°C)	Standard Operative Temperature (°C)		
		3.8 cm/sec (7.5 ft/min)	7.6* cm/sec (15 ft/min)	15.2 cm/sec (30 ft/min)
20	35	22.2	20	17.0
	30	21.5	20	17.9
	25	20.8	20	19.0
25	35	26.5	25	22.9
	30	25.8	25	24.0
30	35	30.7	30	29.0

*Standard Air Movement.

data may be accounted for by the simple observation of air movement present. In direct calorimetry experiments, where control of air movement is obviously precise, the foregoing remarks do not apply; but to those who, with increasing frequency, use conditioned chambers where the air space is always large in relation to the subject, the use of Standard Operative Temperature is specially recommended. As a basis of comparison between the various forms of direct and indirect calorimetry it is recommended to all.

Table 3. Variability of Standard Operative Temperature and its Equivalent Calorie Change with Difference between Skin and Air Temperature at Low Air Movement of Range, 3.8 to 15.2 cm/sec (7.5 to 30 ft/min).

$T_S - T_A$ (°C)	Degree of variation in T_0 (°C)	Equivalent calorie value $K_0 = 7 \frac{\text{Kg} - \text{Cal}}{\text{m}^2/\text{hr}/°\text{C}}$	As % of average metabolism $45 \frac{\text{Kg} - \text{Cal}}{\text{m}^2/\text{hr}/°\text{C}}$
5	1.8	12.6	28
10	3.7	25.9	58
15	5.2	36.4	81

The question of instrumentation has come up many times in the past ten years—how a single physical instrument may be designed to measure as a unit all the various environmental factors. Omitting for the present whether there is a real necessity to include humidity in such a measuring device, let us consider radiant temperature, air temperature, and air movement. Where air movement is relatively constant, it is quite possible to design an instrument that integrates radiant temperature and ambient air temperature, even weighting the relative importance of radiation and convection as does the human body. An instrument reading directly in operative temperature would be the classic globe thermometer, whose surface bears the proper balance between the polished and the blackened to give the desired ratio between the radiation and convection. With the problem of including air movement appears the question of what the proper surface temperature should be if the instrument has its own heat source. An instrument already developed for this purpose is known as the Eupatheoscope (1930) where a constant surface temperature is maintained by an intermittent heater so that the power consumed is a measure of the combined effect of T_W, T_A, and V. Although fundamentally sound, as an instrument, the constancy of surface temperature over all environmental temperatures has no parallel in the skin of the human body, whose temperature may actually change with air movement, because of physiological changes or of the presence of clothing, or of both these factors operating simultaneously. An instrument whose surface temperature response exactly paralleled the response of the human body would, indeed, be a complicated mechanism. Actually, it is impossible to build a simple physical instrument that will serve any practical purpose in integrating wall temperature, air temperature, and air movement in a way that has any valuable physiological application. The Globe Thermometer, the Eupatheoscope, and even the Thermo-Integrator have all served their purpose as educational devices. Their actual usefulness at present is not as originally intended, but lies in their ability to measure such basic factors as radiant temperature and air movement in a well-integrated fashion. For physiological purposes we must measure directly these environmental factors themselves, *i.e.*, air temperature, wall temperature and air movement, and relate them as a whole to a generalized single temperature scale, such as Standard Operative Temperature, applicable in the strict Newtonian sense to the human body.

Summary

The term *operative temperature,* used earlier by the Pierce Laboratory to describe the combined physical effect of wall and air temperature on the human body, is extended to the case where large variations in air movement are also present. In its new generalized form Standard Operative Temperature is defined by the relation

$$\frac{K}{1+K}[T_W]+\frac{1}{1+K}\Big[\left(\sqrt{V/V_0}\right)T_A-\left(\sqrt{V/V_0}-1\right)T_S\Big],$$

where T_W, T_A, and V are the observed wall temperature, air temperature, and air movement, respectively. K represents the ratio of the radiation constant to the convection constant for the chosen standard air movement, V_0. T_S is the observed surface temperature of the human body. The square root relations follow from the fact that the convection loss for the human body is proportional to the square root of air movement. In general the foregoing temperature resulting from the physical combination of T_W, T_A, and V describes an imaginary environment of equal wall and air temperature with standard air movement, V_0, in which the human body, if placed with the observed surface temperature, T_S, would lose the same amount of heat by radiation and convection as in the original environment. Applications of Standard Operative Temperature are made for the nude human subject to data where the ambient air temperature varies from 23 to 35 °C and the air movement varies from 7.6 to 264 cm/second (15 to 520 feet per minute). It is shown how experimentally the fundamental zones of heat regulation follow identical temperature limits on the new generalized temperature scale, as on the earlier operative temperature scale, where data for constant and minimal air movement only were considered. Finally, it may be pointed out that Standard Operative Temperature may also be applicable to experimental animals if a measure of T_S is available.

Discussion

James D. Hardy: Dr. Gagge is to be congratulated on another real contribution to the study of heat regulation in animals. Surely the only way in which observations in one laboratory may be compared to those obtained in another laboratory, under slightly different conditions, is in the way which has been pointed out, that is, by the use of a standard operative temperature. By use of this standard one may, by making simple measurements, separate out the differences in physical environment and discover whether or not there are any actual differences in physiology. Thus the work at the Russell Sage Institute done in a small chamber calorimeter may be compared directly with that done by the investigators of the Pierce Foundation, which is done in an open room with hot and cold walls and electric fans. The practical need of such a reduction of convection and radiation to a standard operative temperature is therefore obvious.

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Temperature Changes in the Muscles of the Human Leg

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Aided by grants from the Council on Physical Therapy of the
American Medical Association.

Experimental Procedure

The use of needle thermocouples permitted the observation of temperature changes occurring in the muscles of the calf of the leg in living human subjects during the application of various procedures. These thermocouples were made of iron-constantan (Leeds and Northrup). They were 5 cm in length and inserted full depth into the calf of the leg. Their accuracy was checked before and after each experiment. Simultaneous determinations of the temperature of the skin surface of the big toe were made by means of iron-constantan surface thermocouples, and of the rectal temperature through the employment of a continuously indicating resistance thermometer.

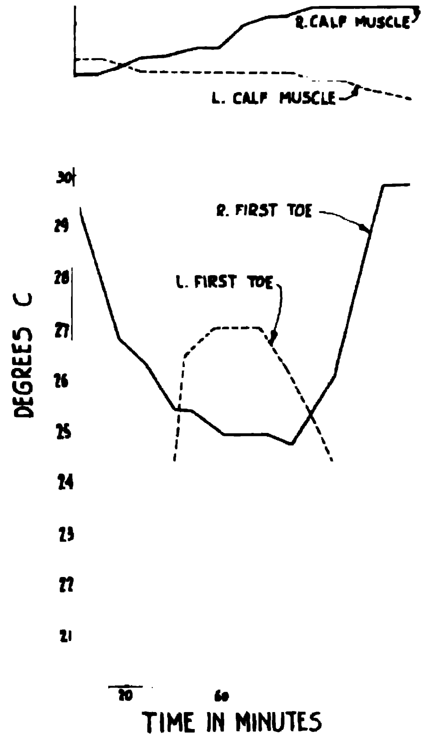

Fig. 1.

Changes in calf muscle and toe temperatures following:

———— Intravenous injection of 2 cc of 1:1000 adrenalin in 33 cc physiologic saline.

---------- Spinal anesthesia.

Data

The following are typical temperature curves. In Fig. 1 are shown changes occurring during spinal anesthesia. The skin surface temperature rose markedly while that of the muscle fell slightly.

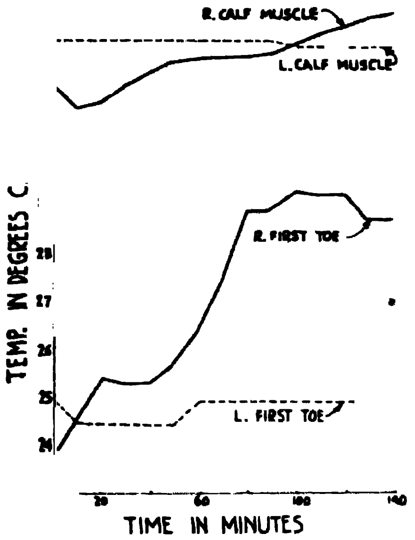

FIG. 2.

Changes in calf muscle and toe temperatures following:

———— Intravenous injection of 300 cc of 5-per cent sodium chloride solution.

---------- Intravenous injection of 300 cc of physiologic saline solution.

Similar changes were found after the paravertebral injection of alcohol. It is plain that paralysis of the sympathetic nerves in the lower extremities causes a vasodilatation of the blood vessels in the skin but no increase in the circulation of the muscles. Fig. 1 also illustrates the influence of adrenalin injected very slowly into the vein by the drop method. The decided fall in skin surface temperature was accompanied by a rise in muscle temperature.

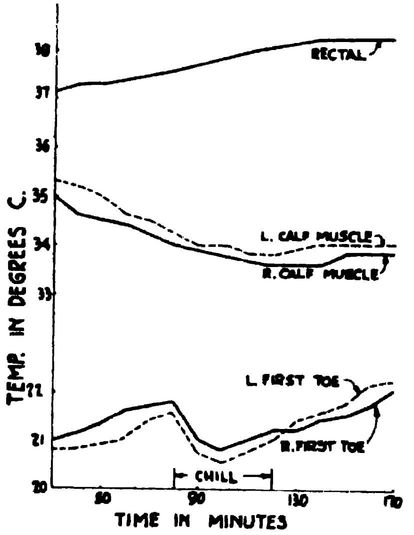

FIG. 3.

Changes in rectal, calf muscle, and skin surface temperatures following a typhoid reaction with chill.

The intravenous administration of 300 cc of 5-per cent sodium chloride solution produced an elevation in both skin and muscle temperatures (Fig. 2). Control observations with an equal quantity of physiologic salt solution failed to cause any temperature changes (Fig. 2).

Typhoid vaccine was injected intravenously in a quantity sufficient to cause a rise in rectal temperature. The calf muscle temperature fell steadily as the rectal temperature rose. The skin surface temperature rose. With the occurrence of a chill, the skin surface temperature fell during the time of the chill (Fig. 3).

When ice bags were placed an either side of the calf, the muscle temperature declined quickly (Fig. 4).

Active exercise produced a rise in muscle temperature and a temporary fall in skin temperature. The changes during passive exercise were similar, but much less marked.

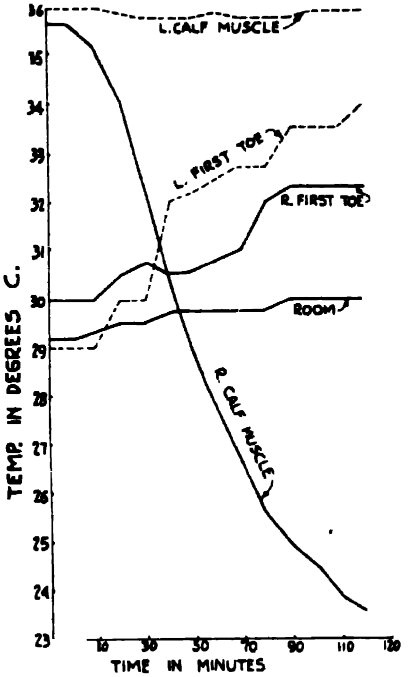

FIG. 4.

Application of ice bag to right calf.

Discussion and Conclusion

By means of thermocouples it is possible to determine independently the temperature changes occurring simultaneously in the skin and in the muscles of the lower extremities. These temperatures are normally lower than those observed in the human torso. We believe that these changes indicate corresponding variations in the blood supply to the extremities. If this reasoning is correct, we are able to evaluate objectively the influence of various chemical and physical measures. This can act as a guide in the treatment of peripheral vascular disease of the lower extremities in the human.

These determinations were made with the coöperation of Drs. M. Friedlander and S. Silbert.

Discussion

James D. Hardy: Dr. Bierman's paper shows in excellent outline how local changes in skin temperature in the hands and feet may be used as indices of blood flow in the extremities. The surface temperature of the fingers and toes serves as a semi-quantitative measure of vasomotor response in these parts, the skin temperature rising as a result of increased blood flow and falling with decreased blood flow. So far as my experience goes, this relationship is general, and in our laboratory we have come to accept these changes in skin temperature in the hands and feet as special reactions essentially unrelated to the adjustment of the body to maintain thermal balance. The hand and foot temperatures, while indicating the blood flow locally, do not say anything concerning the total blood flow over the body surface. This is nicely demonstrated by Dr. Bierman's first slide showing the experiment on epinephrine infusion. The toe temperature falls indicating vasoconstriction and locally decreased blood flow. The temperature of the calf muscle rises with the generally increased superficial blood flow which accompanies epinephrine infusion. Therefore, it should be borne in mind that, whereas the temperature changes in the fingers and toes may parallel the changes in general superficial circulation, they cannot be used for more than an index of the local change in circulation.

It is my feeling that the temperature of the muscle of the calf of the leg cannot be used as Dr. Bierman proposes, that is, as an index of blood flow in the muscle. The fall in muscle temperature in Fig. 1 was probably due not to an altered blood flow but to the cold blood returning from the extremities.

Skin Temperatures of the Extremities Under Various Environmental and Physiological Conditions

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Various investigations made during the past few years indicate that the unclothed or lightly clothed normal individual, in a recumbent position and in still air, exhibits normal physiologic regulation between air temperatures of approximately 24 to 30 °C (75 to 85 °F). Above 30 °C or thereabouts, the individual adapts himself to the environment largely by sweating (zone of evaporative regulation) in order that the balance between heat production and the loss of heat from the body may be maintained. Below approximately 25 °C the skin temperature falls and the heat of the body tissues decreases more or less continuously (zone of body cooling), since the blood vessels of the skin are normally constricted and the body cools as an inanimate object in accordance with Newton's law of cooling. Within the range of atmospheric temperatures extending from approximately 24 to 30 °C, which is referred to frequently as either the zone of comfort or the zone of vasomotor control, blood flow to the skin is changed so that the loss of heat is automatically adjusted to the environment, and there is no sweating or generalized feeling of warmth or cold.

The human body adjusts itself to low environmental temperatures chiefly by vasomotor constriction of the peripheral blood vessels and to high atmospheric temperatures largely by an increase of sweat subsequent to maximal vasodilatation of the peripheral vascular system. As has been shown by the investigations of Burton and Murlin,[3] Burton and Bazett,[4] and Winslow, Herrington and Gagge,[23] the physical regulation is due essentially to a change in conductivity over the gradient between environmental and internal body temperatures brought about by constriction or dilatation of the blood vessels. That various portions of the surface of the body play relatively different roles in the elimination of heat from the body, and that increasing the atmospheric temperature or increasing heat production causes a much greater shift of blood to the extremities was shown by Maddock and Coller,[13] and Herrick and Sheard.[10] In 1939 Sheard, Williams, Roth and Horton[20] reported the results of further investigations regarding the dependence of the dissipation of heat in the zone of vasomotor regulation on the state of vasoconstriction of the peripheral vascular systems and the relative roles of the upper and lower extremities in the control of heat elimination. Although, as is well known, the exchange of heat between the body and its environment takes place over the entire surface of the body, our investigations clearly demonstrated that measurements of the skin temperatures of the fingers and toes serve as the most sensitive indicators of the changes in the vasomotor tone of the superficial vessels (a process which, presumably, occurs over the whole integument) in order that the rate of heat production may equal the rate of heat loss, thereby maintaining approximate constancy of the internal temperature of the body. The regulation of the loss of heat is maintained chiefly by vasomotor control of the peripheral blood vessels and consequent adjustments in the shifts of blood and changes in blood flow to the integument of the extremities.

In this contribution are presented results which were obtained on individuals with normal circulation of the blood when placed under environmental temperatures ranging from 18 to 34 °C (65 to 93 °F) regarding: (1) control of environmental conditions and subjects of test; (2) the effects of posture on the skin temperatures of the extremities; (3) the relationship between basal metabolic rates and the temperatures of the toes under an environmental temperature of 25-25.5 °C (77 to 78 °F) and 40 per cent relative humidity (assumed as standard conditions in all these investigations); (4) the thermal changes produced in the extremities by the ingestion of food; (5) changes in the temperatures of the fingers and toes and the relative roles of the upper and lower extremities in the regulation of the dissipation of heat from the body when the subjects were placed under closely controlled environmental conditions which were changed by increments of 1 to 2 °C within the range of 18 to 34 °C; and (6) the effects of changes of relative humidity on the skin temperatures of the extremities.

Experimental Standards and Criteria

It is necessary that there be satisfactory control and regulation of the atmospheric conditions, the person under test and the physical methods for the measurement of cutaneous temperatures. Details regarding the control of temperatures and humidities, thermocouples and the measurement of skin temperatures are given elsewhere.[19] Air movement was confined to 15 to 30 linear feet per minute with avoidance of drafts. The subjects wore light-weight pajamas or shorts and remained in the horizontal position (slightly elevated) on a comfortable bed for periods which extended frequently from 9 A. M. to 5 P. M.

Period of Adaptation. The necessity of an adequate period of adjustment of the body to any given temperature was shown by Freeman and Lindner;[7] hence it is essential that the body remain under any given atmospheric condition for an hour or more, or until fairly constant readings of the extremities (particularly of the toes) are obtained, in investigations concerned with the effects of environmental conditions on the relative roles played by various portions of the body in the dissipation of heat. Various investigators have found that, when the clothes are removed from the entire body and the skin is exposed to ordinary room temperatures, the skin temperature of the body begins at once to fall and continues to do so from one-half hour to one hour. Cobet and Bramigk[5] found that, in rooms regulated to the range of 23-26 °C, the temperatures of almost all points on the skin were practically constant after about an hour's exposure. Furthermore, the data which we have obtained concerning the rates of heating and cooling of tissues, particularly of the toes, indicate that adjustment to changes in atmospheric temperatures takes place in normal subjects in about an hour's time.

Posture. Roth, Williams and Sheard[18] published in 1938 the results of their investigations on the changes in skin temperatures of the extremities produced by changes in posture. Under environmental temperatures ranging from 23 to 30 °C (73.4 to 86 °F), with the subjects in the basal metabolic state and free from sweating of the extremities, the skin temperatures of the toes and fingers decreased when the extremities were elevated and increased when the extremities were pendent. These changes generally occurred during a period of thirty minutes subsequent to change in posture. Therefore it is quite essential that, in investigations in which measurements of the skin temperatures of the extremities are used as evidence of normal circulation or of peripheral vascular deficiencies, due consideration be given to the time required for adaptation of the body to any change in posture as well as to a change in environmental temperature. These criteria are met when fairly constant temperatures of the toes are obtained over a period of a half hour. The effects of disrobing, of change of environmental temperature which may have occurred when the subject came into the room at 25 °C, and of posture are shown in curves 1 and 2 (toes) of Fig. 1 by reason of the decreases in temperature of the toes during the two hour period from 9 to 11 A. M. The temperatures of the forehead, toes and fingers remain practically constant *per se* from 11 A. M. to 2 P. M, at which time there is an increase in the temperatures of the toes and lower portions of the legs due to the production of heat subsequent to the ingestion of food, as shown in Fig. 20.

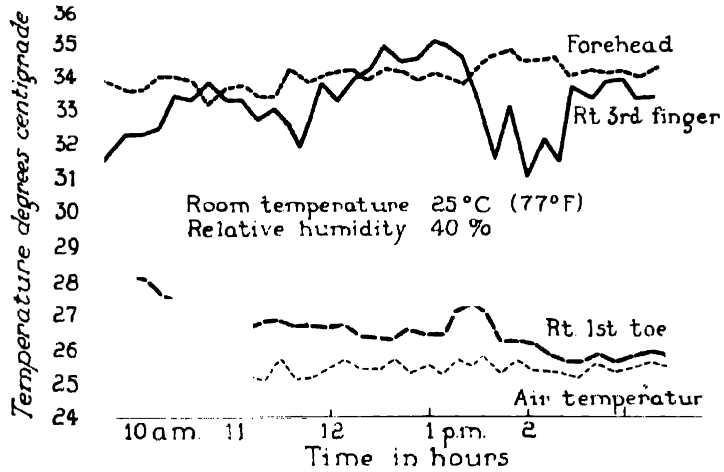

FIG. 1. Curves of the skin temperatures of the forehead, finger and toe of a normal subject in the basal metabolic state in an environmental temperature of 25 °C (77 °F) and 40 per cent relative humidity.

In their recent experiments on the effects of posture on peripheral circulation, Nielson, Herrington and Winslow [16] found that there is a peripheral vasoconstriction over the main surface of the body which is accompanied by a rise in the skin temperatures of the toes. These results are in agreement with our findings. It is probable that the disturbance of the heat-regulating function due to the vasoconstriction in the tilted position (feet down, at an angle of 45 degrees) is compensated by an increase in evaporation.

Hence the maintenance of the subject in the horizontal position and the movement of the bed, subject and thermocouples (which are attached and left in the desired regions throughout the investigations), as a unit, when the effects of changes in environmental temperatures are to be investigated by the use of separate psychrometric rooms maintained at different conditions, have contributed greatly to the accuracy of the data which we have obtained.

Skin Temperatures of the Extremities of Normal Subjects in the Basal State and under Standard (25 °C and 40 per cent Relative Humidity) Environmental Conditions

In clinical investigations concerning functional (vasospastic) or organic (occlusive) involvement in either the upper or lower extremities (or both) and the changes that may be produced by the administration of typhoid vaccine, by increased production of heat through the ingestion of food or by increases in atmospheric temperature, it is necessary to know the relative values of the superficial skin temperatures, particularly of the fingers and toes, of healthy individuals with normal basal metabolic rates, normal dryness of hands and feet, unclothed and in the horizontal position under certain standard environmental conditions. An atmospheric temperature of 25 °C (77 °F) and a 40 per cent relative humidity have been found to be satisfactory, and this environmental standard has been maintained (unless stated to the contrary) in investigations of the skin temperatures of various subjects under these conditions. The skin temperatures of the forehead, thorax and extreme upper portions of the arms and legs of subjects with normal circulation are commensurate in value and lie within the range of 32 °C (89.5 °F) to 35 °C (95 °F). In contrast to these findings, however, there is a peripheral temperature gradient along the extremities extending from the shoulder or thigh to the fingers or toes, as the case may be. The lowest temperatures are exhibited normally by the toes.

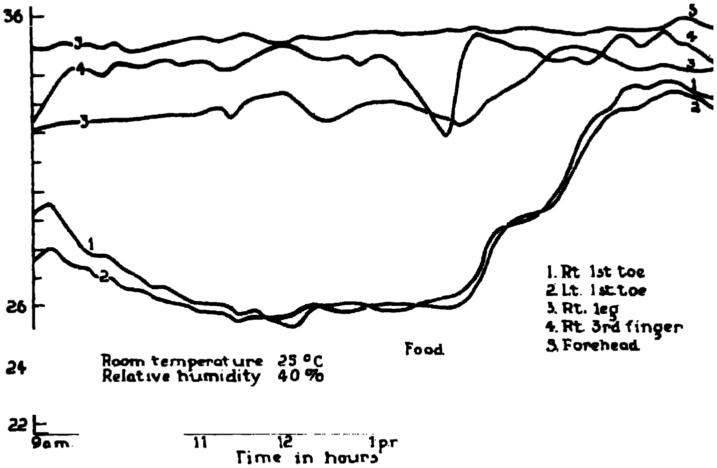

FIG. 2. Curves showing the time-temperature relationship of the forehead, upper leg, fingers and toes of a normal subject before and after the ingestion of food. Curves 1 and 2, indicating the temperatures of the toes, show the rôle of the lower extremities in the control of the dissipation of heat when the subject is in an atmospheric temperature of 25 °C (77 °F), before and after an increase in heat production.

In general, our data show that, in subjects with normal circulation of the blood, approximately maximal vasodilatation of the peripheral vessels of the upper extremities exists in an environmental temperature of 25 to 26 °C (77 to 78 °F) and a relative humidity of 40 per cent. The high degree of vasodilatation of the peripheral vessels of the upper extremities is indicated by the fact that the temperatures of the fingers, which are the most sensitive indicators of the vasomotor regulation occurring in the upper extremities, are at the temperature of the forehead and thorax. On the other hand, the temperatures of the toes are commonly at, or but slightly above, the room temperature, 25 °C (dependent somewhat on the basal metabolic rate, as we shall point out elsewhere), thereby indicating a considerable degree of vasoconstriction in the lower extremities. In such conditions, therefore, the skin temperatures of the toes are the most sensitive or delicate indicators of the regulation of the loss of heat from the body as controlled chiefly by vasoconstriction of the peripheral vascular system of the lower extremities. Hence the finer or more precise control in the exchange of heat between the body and its environment is accomplished by the lower extremities, as is most markedly shown by the skin temperatures of the toes. In the range of vasomotor regulation, the thermostasis of the body is accomplished largely by means of varying the blood flow to the feet. Under the environmental conditions which we have chosen as standard, the finer adjustment or regulation of the dissipation of heat is controlled by the vascular supplies to the lower extremities. These relationships are illustrated by the curves of Figs. 1 and 2.

Relationship between the Increased Production of Heat and the Temperatures of the Extremities

Basal Metabolic Rates and Temperatures of the Toes. The distribution of the blood which may be shifted to the surface from the interior of the body in order to effect greater cooling may be investigated by measurements of skin temperature. Profile curves of the skin temperatures may be drawn, starting with the nude subject and exploring the surface from head to foot, as has been done by Benedict.[1] The temperatures of the toes are always the lowest values obtained on any area of the body. If the environmental conditions are maintained at some comfortable value, such as 25 °C and 40 per cent relative humidity, it is found that the temperatures of the feet are lower in individuals with low metabolism than in persons with high basal rates. An inspection of the data of Table 1 shows that, in a group of six normal subjects, carefully controlled and measured under an environmental temperature of 25.5 °C (78 °F) and 40 per cent relative humidity the temperatures of the toes range from 24.6 to 31.4 °C in individuals whose basal metabolic rates were found to lie between 38.3 and 44.3 Calories per square meter per hour. There is little difference in temperatures of the forehead, thorax, and upper portions of the legs in any of the subjects. The temperatures of the fingers and lower portions of the arms show some correlation with basal rates although, as is to be expected from other considerations, this regulation of the loss of heat under constant environmental conditions is not as great as in the lower extremities, as is evidenced by a temperature range of 6.5 °C (average of the readings of toes on right and left feet, Table 1).

Table 1. Relationships between the Basal Metabolic Rates and the Average Skin Temperatures, °C, of Various Areas of the Body under Constant Environmental Conditions (25 °C and 40 per cent Relative Humidity).

	Basal metabolic rate											
Subject	(%)	Cal/sqm/hr	Forehead	Thorax	Right arm	Left arm	Right finger	Left finger	Right leg	Left leg	Right toes	Left toes
1	−14	38.5	35.5	33.9	34.0	33.8	34.1	34.3	31.7	31.4	24.8	24.6
2	−13	38.3	35.2	34.2	34.4	33.9	33.9	33.0	32.1	32.1	26.0	25.9
3	− 5	39.2	35.0	33.7	32.5	32.4	33.0	32.7	31.0	30.7	25.5	25.1
4	− 4	40.2	35.2	33.8	33.6	33.8	34.8	34.5	32.2	31.7	30.3	29.0
5	− 3	39.9	34.8	33.9	32.7	33.2	32.8	32.3	31.6	31.9	28.5	29.3
6	0	44.3	35.2	33.6	33.7	34.1	34.6	34.5	32.2	31.7	31.0	31.4
Difference (max. and minimum)	−14	6.0	0.7	0.6	1.9	1.7	2.0	2.2	1.2	1.4	6.2	6.8

Kirklin, Plummer and Sheard[12] recently reported their findings regarding measurement of skin temperatures in ten cases of exophthalmic goiter before and after the administration of compound solution of iodine (Lugol's solution) and before and after partial thyroidectomy, under constant environmental conditions of 25 °C and 40 per cent relative humidity. In this series of cases, the average temperature of the toes was 33.4 °C before treatment and operation, and 27.9 °C postoperatively: an average postoperative decrease in temperature of the toes of 5.5 °C. The corresponding average temperatures of the fingers were 35.6 °C and 34.7 °C, indicating an average postoperative change of about 1 °C. The data show that, with reduction of basal metabolic rate, either following partial thyroidectomy or the administration of compound solution of iodine (Lugol's solution), there is a reduction in the temperatures of the toes, and that the temperatures of the toes fall within the range normally expected when the basal metabolic rates are reduced sufficiently to lie at or near the accepted normal values.

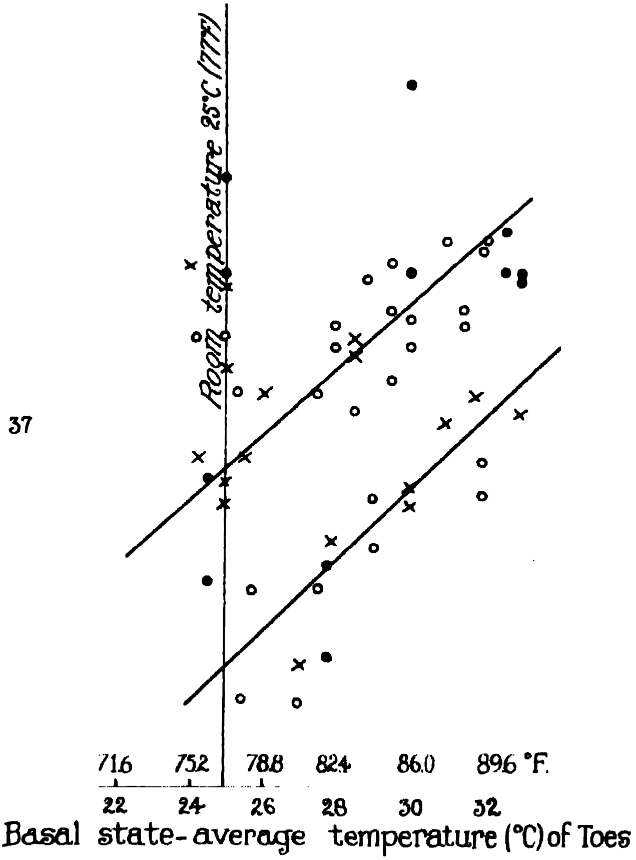

Fig. 3. The relationships between the average temperatures of the toes of a group of normal subjects and the basal metabolic rates. The atmospheric conditions were maintained constant at 25 °C and 40 per cent relative humidity.

Maddock and Coller[13] concluded that the close connection between the temperature of the extremities and the mechanism for the dissipation of heat is shown by the fact that, under constant environmental conditions, a simple linear relationship is found between the temperatures of the great toes and the basal heat production per unit of surface area. The experimental data on which this conclusion of Maddock and Coller is based are meager and open to some criticism. The results of our findings on a group of normal subjects are shown in Fig. 3. The environmental conditions were 25 °C and 40 per cent relative humidity in each test. There is a rather wide scatter of points, but there is evidence to show that an approximately linear relationship (which, however, seems to be of a dual character) exists between the average temperatures of the toes and the basal metabolic rates. We are unable to offer any explanation for this division of subjects into these two groups, since there is no connection between the findings and sex, season of the year, or other factors of this character. However, the type (slender or stout) of the individual, and the presence of sweat on the extremities or normally dry feet and hands as the case may be, may offer some possible explanation.

These data emphasize the important roles played by the extremities, particularly the lower portions of the legs and feet, in the regulation of the dissipation of heat from the body, and add evidence to the statement that the thermostasis of the body is effected largely by means of varying the blood flow to the lower extremities when the body is in the zone of vasomotor regulation and body cooling.

The Ingestion of Food. The necessity of basal conditions is emphasized when investigations are to be made on the so-called specific dynamic action of foods or in the determination of the thermal changes produced in various areas of the body subsequent to the ingestion of food and, in particular, in a comparison of the temperatures of the fingers and toes of individuals with normality of circulation and those with peripheral vascular disease. After a fast of from twelve to eighteen hours and after the temperatures in the various areas of the body under test remained constant to within approximately 1 °C, the subject ate a meal which was balanced in essential types of food and furnished approximately 600 Calories. In all instances, the temperature of the forehead remained constant within 1 to 1.5 °C throughout the day. In general, shortly after the ingestion of food, the temperatures of the fingers, wrist and upper leg rise to their maximal values (approximately that of the forehead) when the room temperature is 25 °C.

In order that the data regarding the changes in skin temperature of a normal subject after the ingestion of food may be available for comparison with the results obtained on persons with peripheral vascular diseases, and to point out the relative roles played by the upper and lower extremities in the dissipation of heat and the influence of environmental conditions on these relative roles, we are including two rather characteristic sets of results on normal subjects in Figs. 2 and 4.

The data plotted in the left-hand portion of Fig. 2 (from 9 A. M. to 1 P. M.) show that, in a person in the basal state and in an atmosphere of 25 °C (77 °F), the temperatures of the fingers and forehead were approximately 34 to 35 °C (93.2 to 95 °F), whereas the toes were at or near room temperature. These skin temperatures are indicators of approximately maximal peripheral vasodilatation in the upper extremities, with normal vasoconstriction in the feet and lower part of the legs. Hence the regulation of the elimination of heat should be assumed by the lower extremities in the event that the production of heat is increased, as through the ingestion of food, and the thermal changes of the toes should vary somewhat commensurately with changes in the rate of heat production. This is shown by the considerable rise in temperature of the toes of both feet (from 26 °C, curves 1 and 2, Fig. 2) in the course of three hours after ingestion of a standard meal.

The curves of Fig. 4 give the time-temperature relationships for the forehead, wrist, finger, leg and toe of another subject who, after fasting fifteen hours, was placed in a room at 25 °C (77 °F) and, after two and a half hours, was removed into an environmental temperature of 20 °C (68 °F). About two and a half hours later (between 2 and 3 P. M., and after a total fast of twenty hours), the subject ate a meal. The data on the temperatures in various regions of the body are plotted in the right-hand portion of Fig. 4. Even after the ingestion of a substantial meal, the temperatures of the toes continued at or slightly below room temperature. In contrast, however, there were marked rises in the temperatures of the lower portions of the arms, as is shown by the wrists and fingers, thus indicating increased flow of blood to the upper extremities. From this evidence it may be concluded that, under the environmental conditions specified, the regulation of the loss of heat from the body and the maintenance of constancy of internal temperature were accompanied chiefly by vasomotor regulation of the peripheral vascular system of the forearms and hands.

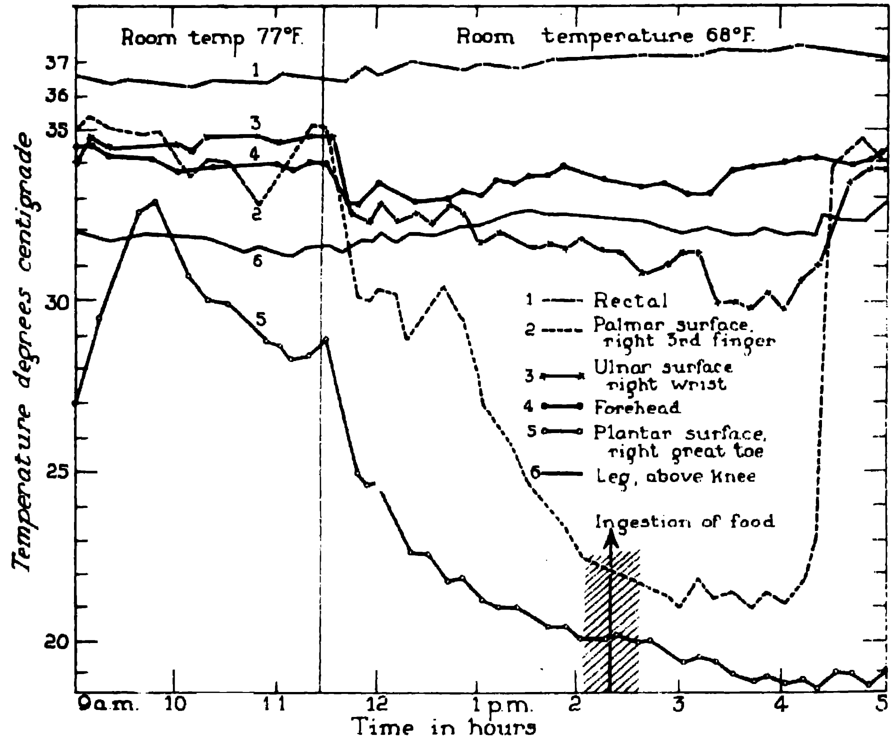

FIG. 4. Changes in the skin temperatures of the legs, wrists, fingers, toes and forehead of a normal male, in the basal state, produced by changes in environmental temperature and after ingestion of food.

The onset of the initial change in temperature of any extremity following the ingestion of food, the maximal value attained, and the duration of the cycle of the change of temperatures of the extremities vary with different individuals (depending on the basal metabolic rate) and the dry-bulb temperature of the environment. In general, it may be stated that the temperatures of the fingers, and therefore of the upper extremities as a whole, must rise to their approximate maximal values (which are about the same as the values obtained on the forehead) before the thermostatic control is taken up primarily by the lower extremities. Also, there may be more than one cycle in the rise and fall of temperature of the toes during a six-hour period following the ingestion of food under environmental and basal conditions which require the regulatory control to be exercised by the lower extremities. In general, the blood pressures increase 5 to 15 per cent and the pulse rates are augmented 10 to 20 per cent shortly after the ingestion of food. These changes varied in their periods of duration, but in general decreased within an hour or two to the values previously maintained.

These results confirm the general trend of conclusions reached in other investigations (Burton and Murlin).[3] The changes in surface temperatures of the body, particularly in the extremities, subsequent to the ingestion of food are indicative of increased rate in blood flow or decreased time of circulation. The investigations concerning the superficial thermal changes in man find their counterpart and physiologic explanation, in part at least, in the work of Herrick, Essex, Mann and Baldes[9] regarding the effect of digestion on the blood flow in certain vessels of the dog, and in the investigations of McCracken, Essex and Sheard[14] on the circulation time of the blood before and after ingestion of food. These researches show that there is a very definite increase in the rate of blood flow and a marked decrease in the circulation time at the height of digestion.

Relative Roles of the Extremities in the Dissipation of Heat under Various Environmental Conditions

The relative role of the upper and lower extremities, as indicated by the skin temperatures of the fingers and toes, in the regulation of the dissipation of heat from the body has been investigated in considerable detail in several individuals with normal circulation under dry-bulb temperatures which have been increased by increments of 1 to 2 °C, the relative humidity remaining 40 per cent. Table 2 presents the data concerning the temperatures of the forehead, upper part of the

Table 2. Skin Temperatures of Selected Areas of the Body of Normal Subjects in the Basal State under Environmental Temperatures Maintained at Various Degrees (Relative Humidity, 40 per cent).*

	Room temp.		Range of skin temperature (°C)			
Subject	(°C)	(°F)	Forehead	Leg (above knee)	Fingers	Toes
A	19.6	67.3	32.3–32.9	32.9–35.4	31.4–32.8	18.6–19.2
	21.1	70.0	33.2–33.4	31.7–32.8	32.2–34.3	20.7–22.9
	22.8	72.9	32.7–33.8	32.4–33.2	33.5–34.6	24.2–26.3
	25.3	77.5	34.3–34.7	33.4–34.0	33.9–34.4	27.6–28.9
	26.0	79.0	34.6–34.9	33.6–34.2	34.6–35.1	30.5–31.6
	26.6	79.8	34.2–35.0	32.9–33.9	34.5–36.2	32.7–33.8
	29.0	84.0	34.6–35.2	34.4–35.1	34.7–35.5	33.9–35.0
	34.1	93.5	35.7–36.2	34.9–35.4	34.5–36.4	35.2–35.7
	18.0	64.5	32.6–32.8	29.5–31.9	23.8–27.9	17.1–18.2
	20.5	69.0	34.0–34.7	30.2–31.4	27.5–30.3	18.6–19.3
	21.0	69.8	33.8–34.2	30.9–32.6	31.3–34.2	19.9–20.6
	22.5	72.5	34.0–34.2	31.3–32.9	33.4–33.9	21.4–21.9
	23.6	74.5	33.8–34.3	32.4–33.2	32.6–34.0	21.8–23.2
	24.5	76.0	33.6–34.5	33.1–33.9	33.2–34.6	23.5–26.1
	25.0	77.0	34.7–35.2	32.7–34.0	35.2–35.8	27.9–29.7
	26.0	78.8	34.1–34.9	33.2–34.1	34.9–36.2	30.6–32.8
	29.2	84.5	34.6–35.3	33.6–34.3	35.3–36.0	32.9–33.7
	32.4	90.4	35.4–36.1	34.9–35.4	35.3–36.4	34.2–35.5

*The range of skin temperatures for any of the specified areas occurred during a period of observation of four to six hours.

leg, fingers and toes of two subjects systematically tested under room temperatures ranging from 18 to 34 °C (64.5 to 93.2 °F). The basal metabolic rates of subjects A and B were 40.7 and 35.9 Calories per square meter per hour, respectively. The range of variation of temperatures for the four areas given in the table occurred in each instance during a period of four to six hours' exposure to the specified atmospheric temperature. The relationships between the room temperatures and the temperatures of the toes and fingers for two subjects of somewhat different basal metabolic rates (difference of 4.9 Calories per square meter per hour) are shown in Fig. 5.

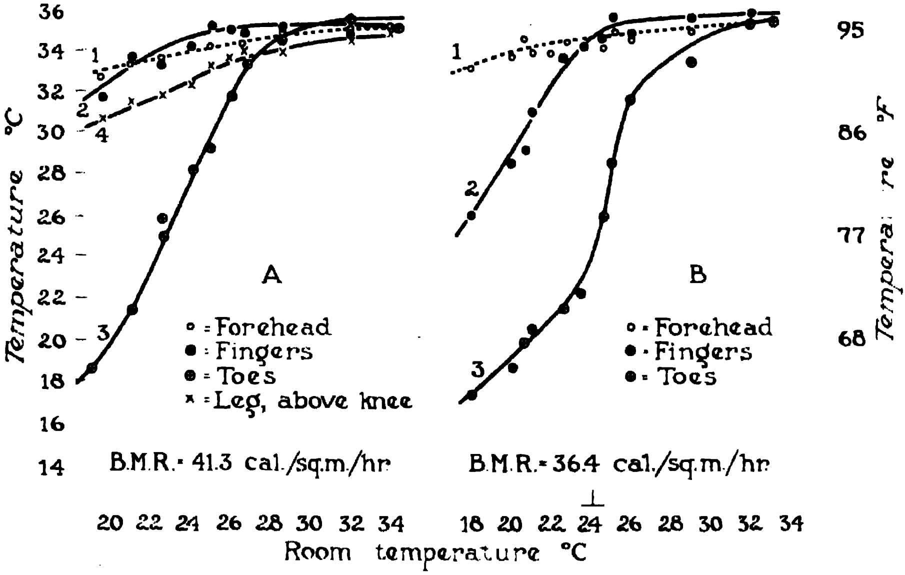

FIG. 5. Curves showing the relative roles of the upper and lower extremities, as indicated by the skin temperatures of the fingers and toes, of normal subjects under a range of environmental temperatures extending from 18 °C (65 °F) to 35 °C (94 °F). Basal metabolic rates: *A*, 41.3 and *B*, 36.4 calories per square meter per hour.

Under environmental conditions ranging from 18 to 22.5 °C (64.5 to 72.5 °F) the temperatures of the toes are, in general, at or near atmospheric temperature, whereas increased vasodilatation is occurring in the upper extremities, as is indicated by the rise in temperature of the fingers. When the fingers reach temperatures of 34 to 35 °C (93 to 95 °F), indicating approximately normal vasodilatation, the temperatures of the toes generally exceed the environmental temperature. This ordinarily occurs at a room temperature of 25 to 26 °C. Further increases in the environmental temperature produce little if any change in the temperatures of the fingers, whereas the temperatures of the toes increase rapidly and reach a value comparable to the temperatures of the fingers under an environmental temperature of 28 °C (82.5 °F) to 29 °C (84 °F). Hence, in normally reacting subjects, as the environmental temperature is increased the regulation of the loss of heat is taken care of, initially, by the hands and lower portions of the arms, since normal vasoconstriction of the lower extremities and particularly of the feet is present. This is followed by a regulatory control on the part of the feet and lower portions of the legs when the room temperature reaches 25 °C (77 °F). Finally, at higher environmental temperatures (28 to 30 °C, or 82.5 to 86 °F), the temperatures of the toes closely approximate the temperatures of the forehead, thorax, legs, arms and fingers. At temperatures exceeding about 31 to 32 °C, maximal vasodilatation of peripheral blood vessels will be maintained, peripheral blood flow will increase proportionately with the temperature, and the internal temperature of the body will be kept approximately constant by changes in secretion of sweat, and the chief regulation or control in the elimination of heat will be by evaporation.

Bedford [2] took the skin temperatures on the forehead and palm of the hand of over 2000 industrial employees by means of a Moll thermopile, and on the foot by means of a thermocouple when the subjects were in temperatures ranging from 12 to 24 °C. On the average, the temperature of the forehead rose 0.139 °C for a rise of 1 °C in the air temperature. The temperature of the palm rose 0.465 °C and that of the foot 0.806 °C for each degree C rise of air temperature. Our data on the fingers, obtained on nearly nude subjects in environmental temperatures of 20 to 26 °C, showed an average rate of rise of 0.62 °C in six individuals for 1 °C rise in room temperature. The toes showed an average rate of rise of 2.35 °C for each 1 °C increase in room temperatures within the range of 20 to 26 °C. The differences in response of the extremities *per se*, and the difference between rate of temperature change of the extremities and the forehead illustrate the significant part played by the extremities, and in particular by the lower extremities, when the body is in the zone of vasomotor regulation.

Relative Humidity and Skin Temperatures of the Extremities

In his review of the subject of skin temperature and its significance Murlin [15] wrote: "So much does one hear through popular channels of the effects of humidity on comfort, health and happiness, and so vivid are one's experiences of its effects at both extremes of temperature, that one is prepared to learn that humidity is quite as important as atmospheric temperature itself in determining the temperature of the skin from which the familiar sensations arise. The reality is quite otherwise."

In 1931 Talbot,[21] in a very complete report on skin temperatures of children, stated: "In the series of measurements made on ten subjects at room temperatures of 20 to 22.5 °C, there were no consistent changes in the skin temperature over different parts of the body when the humidity varied from 31 to 90 per cent." Phelps and Vold [17] found that it would require an increase of 50 per cent in the relative humidity, say from 30 to 80 per cent, to raise the skin temperature 0.5 °C.

Using unclothed subjects, Winslow, Herrington and Gagge [24] found that the relative humidity had very little effect on comfort in the zone of vasomotor control and body cooling (below about 29 °C). Below an air temperature of 25 °C (77 °F) the secretion of sweat is at a minimum for the clothed, semi-reclining body, and variations downward in the relative humidity of the atmosphere exert only a minor effect on loss of heat by evaporation. With low movement of air and low relative humidity, the evaporative heat loss is about 4 kg-calories per square meter per hour (1.5 B. T. U. per square foot) greater than with a relative humidity of 75 to 80 per cent. This is equivalent to a change of less than 1 °F in the air temperature.

The reason why the relative humidity of the atmosphere exerts little effect on the loss of heat by evaporation when the body is in the zone of vasomotor regulation and body cooling is purely a matter of physics, as has been emphasized recently by Hardy and DuBois.[6,8] The vapor pressure at the surface of the skin at 33 °C (91 °F) is 1.47 inches of mercury, whereas in air at 21 °C (70 °F), with a saturation of 80 per cent, it is only 0.58 inch, or a gradient which permits the full evaporative loss.

In our investigations regarding the relative roles of the upper and lower extremities in the dissipation of heat from the body, as judged by the temperatures of the fingers and toes, the relative humidity was maintained as near 40 per cent as possible. It was of interest, therefore, to determine whether changes in relative humidity at any specified air temperature produced changes in the temperatures of the fingers and toes (since thermal changes of the fingers and toes are the most sensitive or delicate indicators of change in vasomotor control and thermostatic regulation) of two normal subjects with basal metabolic rates of 44.5 and 39.2 Calories per square meter per hour. A range of air temperatures from 21 °C (70 °F) to 27.5 °C (82 °F) was chosen because the loss of heat due to evaporation is nearly constant (approximately 25 per cent) and the subjects reported comfort except for some chilliness of feet at the lowest environmental temperature. Furthermore, the changes in the temperatures of the toes are of the greatest significance since, within the specified range of dry-bulb temperatures, the temperatures of the forehead, thorax and upper portions of the legs are commensurate and high in value, and the upper extremities (as evidenced by the temperatures of the fingers) are involved but little in the regulation of dissipation of heat.

The data recorded in Table 3 show that, within the range of normal variations of environmental and skin temperatures, there is little if any effect of considerable changes in relative humidity at any given dry-bulb temperature (21° to 28 °C) on the skin temperatures of the fingers and toes. Any minor increases in skin temperature which may be produced by large increases in atmospheric humidity are overshadowed by the relatively large temperature changes in the extremities (particularly feet and toes) due to small changes in environmental temperature. Hence, in the zone of comfort or vasomotor regulation and body cooling, the dissipation of heat from the body is dependent chiefly on the environmental temperature and is little influenced by relative humidity, when the person under test is in the basal state, lightly clothed and at rest in still air.

Table 3. Data Regarding the Skin Temperatures of the Fingers and Toes of Subjects Placed under Specified Environmental Temperatures and Various Relative Humidities.

Environmental conditions		Subject C		Subject D	
Dry-bulb temp.	Relative humidity (average value) (%)	Average temp. (°C) Fingers	Toes	Average temp. (°C) Fingers	Toes
21 °C	50	31.5	22.4	30.2	21.7
(70 °F)	78	28.4	22.9	28.6	22.1
22.2 °C	40	29.3	23.8	28.5	22.2
(72 °F)	65	30.5	25.4	31.0	23.9
23.3 °C	40	34.8	30.1	33.8	29.5
(74 °F)	54	33.2	27.5	32.7	26.4
	68	29.8	24.9	29.5	25.9
24.5° C	38	34.7	29.5	33.5	28.7
(76° F)	55	34.3	30.0	33.8	28.9
	73	34.6	29.3	34.5	29.4
26.1 °C	35	35.4	32.4	35.6	32.4
(79 °F)	50	35.2	32.1	35.0	32.9
	64	35.9	33.5	35.7	34.0
27.8 °C	34	35.6	34.0	35.6	34.3
(82 °F)	55	35.0	34.5	36.2	34.0
	78	35.4	33.6	35.4	33.5

Williams, Horton and Sheard[22] investigated the changes in skin temperatures (chiefly of the fingers and toes) of normal subjects under various environmental conditions which ranged from 66 to 77 °F on the effective temperature scale proposed by Houghten and Yagloglou.[11] Effective temperature is defined as "the temperature and humidity condition, or the heat and moisture condition, of the air which determines the transfer of heat between it and the body." For example, an effective temperature of 71° on the Fahrenheit scale may be made up of various equivalent dry-bulb temperatures and relative humidities, as 78 °F and 40 per cent relative humidity, 76 °F and 50 per cent relative humidity, or 74 °F and 65 per cent relative humidity. At 71 E. T. the average temperature of the toes was found to be 26 °C or 79 °F when the dry-bulb temperature was 74 °F, with a relative humidity of 65 per cent, and was 32 °C (89 °F) when the air temperature was 79 °F with a relative humidity of 35 to 40 per cent. The various sets of data thus obtained further demonstrate that, within the range of environmental conditions in which the lower extremities play the chief role in the regulation of the dissipation of heat as indicated by the skin temperatures of the toes, there is little effect of considerable changes in the wet-bulb temperatures in contradistinction to the definite influence of relatively small changes in dry-bulb temperature.

In conclusion, these investigations emphasize the fact that the amount of heat to be lost in order to maintain constancy of the normal internal temperature of the body, and the temperature of the environment into which this energy is to be dissipated are the two chief factors which control the temperatures of various parts of the body if air movement is kept at a low value. Measurements of changes in skin temperatures of various areas of the body, under controlled environmental dry-bulb temperatures, but with wide range of relative humidities, show that the various portions of the body play relatively different roles in the elimination of heat from the body. Within the range of atmospheric temperatures, frequently referred to as the zone of comfort and extending approximately from 23 to 30 °C (73 to 86 °F), the regulation of the dissipation of heat is accomplished and controlled chiefly by the sympathetic nervous system through the production of vasocontriction or vasodilatation of the peripheral vascular systems of the upper and lower extremities. While the exchange of heat between the body and its environment takes place over the entire surface of the body, the regulation or thermostatic control of the loss of heat is maintained by shifts of blood and changes in blood flow to the integument of the extremities. The temperatures of the fingers and toes are the most sensitive indicators of the changes in the peripheral blood flow to the extremities and of the vasomotor control in order to maintain adequate adjustment of heat exchange.

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Normal Vasoconstriction, Vasospasm and Environmental Temperature

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The discovery of the vasomotor nerves by Claude Bernard[1] was an event of outstanding scientific importance. In 1851 Bernard announced that cutting one sympathetic nerve in the neck of a rabbit brought about a dilatation of the blood vessels of the ear and an elevation of surface temperature on the corresponding side. Application of these investigations to the treatment of diseases of the peripheral arteries was slow to develop. The surgery of the past decade has demonstrated that the removal of the sympathetic innervation to the extremities of the human body is followed by permanent vasodilatation of the arteries to the extremities. The introduction of operative procedures and various treatments of peripheral vascular diseases made apparent the need for more accurate diagnoses and a better understanding of the pathologic physiology of these diseases.[2,3] Few subjects in physiology are of greater importance to the physician than that of vasomotor regulation. Renewed interest in the skin temperatures of the extremities as criteria of circulation in vascular diseases has brought to light many interesting and valuable facts.[4,6]

Normal Vasoconstriction and Vasomotor Regulation

In another communication[7] we pointed out that measurements of changes in skin temperatures of various areas of the body, under controlled environmental dry-bulb temperatures and with a considerable range of relative humidities, show that the various portions of the body play relatively different roles in the elimination of heat from the body. Within the range of atmospheric temperatures, frequently referred to as the zone of comfort and extending from approximately 23 to 30 °C (73 to 86 °F), the regulation of the dissipation of heat is accomplished and controlled chiefly by the sympathetic nervous system through the production of vasoconstriction or vasodilatation of the upper and lower extremities. The temperatures of the fingers and toes are the most sensitive indicators of the changes in peripheral blood flow to the extremities. We have shown that posture, metabolic rate and environmental temperature have considerable effect on the skin temperatures of the fingers and toes and that it is necessary that those factors be controlled carefully if conclusions are to be drawn concerning normal vasoconstriction or vasomotor spasm.

A great deal of confusion has arisen in clinical literature regarding the differentiation between normal vasoconstriction and that due to peripheral vascular disease. In the normal subject there is a fundamental difference in the vasomotor reactions of the hands and feet; there is a distinct vasomotor gradient which exists between the face, hands and feet. The minimal degree of vasoconstriction is in the face, whereas increasing degrees occur in the hands and feet. When, for example, an individual with normal circulation is gradually (by successive stages of 2 °C and at least two hours' exposure to any given environmental temperature) changed from a room temperature of 27 °C (80.5 °F) to one of 23 °C (73.4 °F), the vasoconstriction occurs first in the toes (a decrease of about 10 °C) and finally in the fingers (a decrease of 2 to 3 °C), with only a degree or two of change in the temperature of the forehead. Similar results are obtained regarding the rates of vasodilatation in the hands and feet of subjects placed under standard atmospheric condition (25 °C and 40 per cent relative humidity) after oral administration of alcohol to normal subjects (Horton, Sheard and Roth).[5]

Vasospasm and Skin Temperatures of the Extremities in Peripheral Vascular Disease

The term *vasospasm* is used to indicate spasm in the vessels which is superimposed on the normal degree of vasoconstriction that is present in the peripheral vascular systems. In certain types of peripheral vascular disease (for example, thrombo-angiitis obliterans), the so-called superimposed vasospasm has been given considerable attention. In such conditions, some of this vasospasm may be normal vasoconstriction. Just how much is normal vasoconstriction and how much is vasospasm can be determined only through studies of the peripheral blood flow, as evidenced by skin temperatures, of such subjects in relation to environmental conditions and heat production (for example, the ingestion of food) and by subsequent comparison with the data obtained on normal individuals having practically the same basal metabolic rate.

The difference between normal vasoconstriction and vasospasm can be demonstrated readily if a comparison is made of data on the temperatures of the fingers and toes of three types of individuals: a normal subject, a subject with thrombo-angiitis obliterans and one with Raynaud's disease. If these three subjects (of nearly the same basal metabolism) are placed under a controlled temperature of 20 °C (68 °F) and 40 per cent relative humidity, a striking difference will be shown in the way in which vasodilatation occurs in the hands and feet as the environmental temperature is gradually increased to 32.5 °C (90 °F). In the environment of 68 °F (20 °C) the temperature of the toes of all three subjects will approximate that of the room, and the temperatures of the fingers may also (especially in Raynaud's disease) approximate room temperature and, in that event, show considerable contrast to the normal reactions. As the environmental temperature is gradually elevated, complete vasodilatation will take place in the hands, with considerable vasodilatation frequently present in the feet, when the room temperature reaches 26 °C (79 °F). In contrast to these findings, it will be necessary to continue to elevate the environmental temperature to 29 or 30 °C (84 to 86 °F) or even higher before vasodilatation will occur in the hands and feet of the subject with thrombo-angiitis obliterans. Frequently, higher environmental temperatures are necessary before complete vasodilatation will occur in the digits of subjects with Raynaud's disease. In all three conditions, however, vasodilatation occurs first of all in the hands and then in the feet. In cases of Raynaud's disease we have noted that the temperatures of the fingers were below the temperatures of the toes, and yet vasodilatation invariably occurred more rapidly and at a lower level of environmental temperature than in the toes. These and similar observations show that the degree of vasoconstriction in individuals having peripheral vascular disease is greater than in normal subjects. The difference between the environmental temperatures at which maximal vasodilatation occurs in normal subjects and in individuals with thrombo-angiitis obliterans and Raynaud's disease is an index of the degree of superimposed vasospasm which is present. After sympathectomy, normal vasoconstriction and vasospasm are eliminated from the denervated extremity.

Vasospasm, Occlusion and Environmental Temperatures

In general terms, peripheral vascular diseases may be classified in two main groups: (1) functional diseases, of which Raynaud's disease is an example of the vasoconstrictive type, and (2) organic disease, of which thrombo-angiitis obliterans represents an occlusive arterial disease of the extremities in which some degree of superimposed spasm is usually present in the collateral vessels, especially in the early course of the disease. In these individuals, as in normal persons, the processes of dissipation of heat should occur with a limitation, which is imposed by reason of the inability of the blood vessels to contract or to dilate normally.

Although we have pointed out in general terms in preceding paragraphs that considerable clinical information regarding the character of the involvement may be acquired from studies of the skin temperatures under various environmental conditions, we are adding as illustrative cases the following:

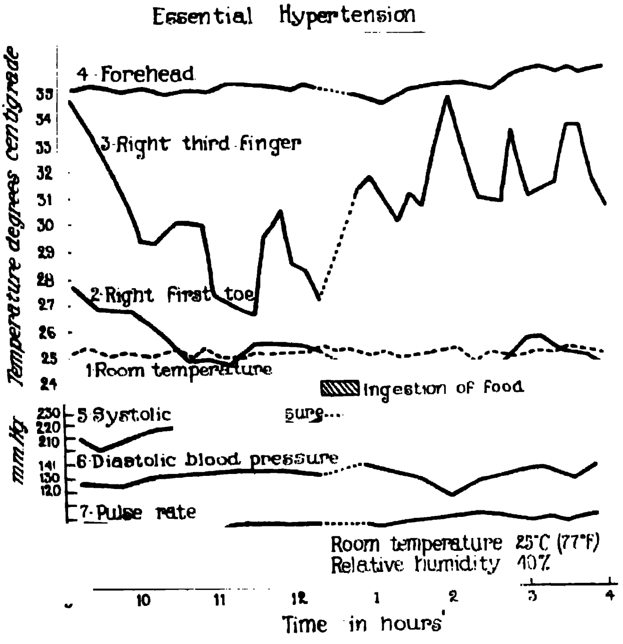

FIG. 1. Essential hypertension. Curves showing the time-temperature relationships of the forehead, fingers and toes in an environment of 25 °C. The temperatures of the fingers and toes indicate abnormal vasoconstriction.

Case 1.—(Essential hypertension). The patient (Fig. 1) had a blood pressure of 220/130 mm of mercury. There was abnormal vasoconstriction or vasospasm of both extremities, as was evidenced by the fact that the skin temperatures of the fingers were low (ranging from 28 to 32 °C) and vacillated considerably. After ingestion of food, the temperatures of the toes remained at room temperature (25 °C or 77 °F) with some rise in, but spasmodic control of, the temperatures of the fingers and wrists. In an individual of this type there will be, in general, considerable vasodilatation of the extremities when the environmental temperature is raised from 25 to 29-31 °C (84-88 °F). Under such atmospheric conditions, the temperatures of the fingers approximate those obtained with normal subjects and there will be a considerable vasodilatation of the lower extremities, although the temperatures of the toes may be several degrees below the findings on normal subjects in corresponding atmospheric temperatures. However, at room temperatures in the neighborhood of 84 to 88 °F the temperatures of the toes, in general, will rise above the environmental temperature, thus indicating some degree of vasodilatation and increase of blood flow to the extremities involved.

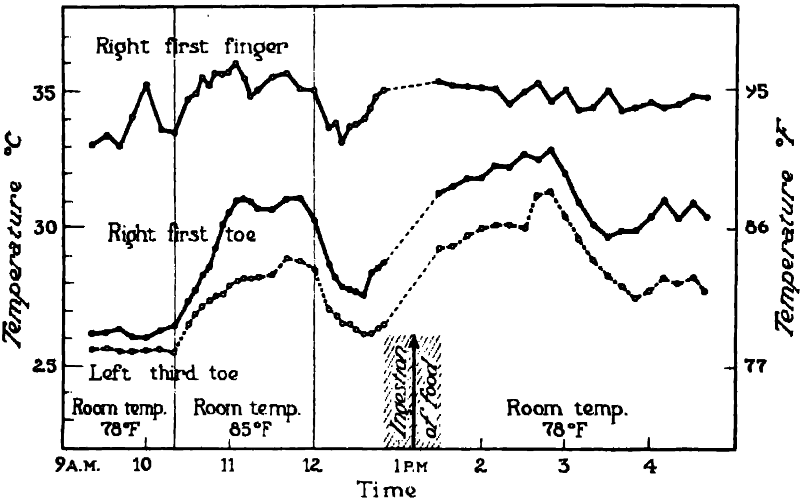

FIG. 2. Thrombo-angiitis obliterans. Curves showing the effects of changes in environmental temperature and the ingestion of food on the surface temperatures of the fingers and toes.

Case 2.—(Thrombo-angiitis obliterans). Fig. 2 shows the effects of the ingestion of food and of changes in environmental temperature on the skin temperatures of the fingers and toes. In this case the effects were confined chiefly to the lower extremities and were more marked in the left lower extremity. The surface temperatures of the fingers were normal, and the temperatures of the toes were approximately at room temperature, 25.5 °C (78 °F). After a period of observation of one and a quarter hours, the patient was placed in an environmental temperature of 30 °C (85 °F); the surface temperatures of the toes of the right foot rose to approximately 31 °C. The temperatures of the left foot rose to 29 °C, thus remaining about 1 °C below the atmospheric temperature. These data show that there is little if any change in the peripheral blood flow to the extremities, and that the rise in the temperatures is due chiefly to heating of the tissue by the environment. It is also obvious that there is a greater degree of occlusion in the left lower extremity. The subject was returned to an environmental temperature of 25.5 °C (78 °F). After the lapse of approximately an hour, food was ingested with a resultant vasodilatation in the digits of the lower extremities. This vasodilatation was more marked in the right than in the left extremity, as is indicated by the skin temperatures of the toes. Either an environmental temperature of 85 °F or the ingestion of food in a room at 78 °F produced some degree of vasodilatation of the lower extremities, but the effects were not comparable to the results obtained when normal persons are subjected to these physical and physiological changes.

A similar study of the skin temperatures of the fingers and toes was made following a left lumbar sympathetic ganglionectomy and trunk resection. In an environmental temperature of 25.5 °C (78 °F) the temperatures of the toes of the left foot were approximately 35 °C (comparable to the temperatures of the forehead and thorax), whereas the temperatures of the toes on the right foot were approximately 27 °C. When the room temperature was 20 °C (68 °F) marked vasoconstriction was observed in the fingers and in the toes of the right foot, whereas the toes of the left foot remained warm and at about 35 °C. When the patient was later transferred to a room at 30 °C (86 °F), no appreciable changes in the temperatures of the toes of the left foot occurred (since maximal vasodilatation following the sympathectomy had been produced) but there was a marked rise in the surface temperature of the toes of the right foot. The temperatures of the toes on the right foot, however, still remained approximately 5 °C lower than those of the toes of the left (operated side) foot. This shows that vasospasm disappears from the denervated extremity and that, after denervation, there are no reactions to changes in environmental temperature within the limits of 78 to 86 °F.

Comment

Atmospheric temperatures may be found under which considerable dilatation of the peripheral vessels occurs in functional vasospasm. In general, there will be corresponding changes in the temperature of the toes commensurate with the values found in normal subjects, although conditions are encountered in which there is evidence of tissue heating with but little vasodilatation of the blood vessels. In organic occlusion of the lower extremities with some superimposed spasm, environmental temperatures may be established in which the temperatures of the toes will be above atmospheric temperatures, thereby indicating increased blood supply.

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Observations on Human Beings With Cancer, Maintained at Reduced Temperatures of 75-90° Fahrenheit

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During a little more than three years the authors have been interested in observing the effects of reduced temperatures upon embryonal cell growth and activity, especially in its possible application clinically to the cancer field. These observations have included studies upon chick embryos, various forms of plant life and tissue cultures, as well as upon hopeless cases of human cancer.

It has been shown by Fay and Henny[1] that the prolonged local application of temperatures of 40-50 °F to human neoplastic lesions resulted regularly in the relief of pain and in reduction of the size of the tumor. In these initial studies, carefully controlled temperature readings by means of an extremely accurate and rapidly recording thermocouple (Henny) were obtained. Subsequently, similar skin temperature readings were made in cases where the entire body temperature was reduced, in an effort to maintain levels at least comparable to those found normally existing in the extremities; *i.e.*, 86-88 °F. The rationale for this procedure is explained on the basis of the comparative infrequency of either primary or secondary neoplastic lesions below the elbows or knees, where the only apparent difference from other portions of the body lies in the lower temperature existant.

It was felt that this level of approximately 90 °F must represent a subcritical level in respect to embryonal cell growth. Huggins and Noonan[2] had already suggested that 95 °F was the necessary critical level for normal embryonal cell growth in their classical experiments relating to the bone marrow of white rats. To determine this point as a broad biologic principle, Smith[3] carried out extensive studies upon chick embryos. It was definitely established that 95 °F represented the "critical" level for the normal growth pattern in chicks, and that temperatures between 90 and 95 °F, even for as brief a period as 48 to 72 hours, if applied to chicks at the outset of their incubation, would result regularly in deformities. On the other hand, if cell differentiation was established by incubation at normal levels for this same initial 48- to 72-hour period, then these changes were found only occasionally, even if a 48- to 96-hour subcritical temperature period was introduced later in the course of incubation. Similar results were obtained in preliminary tissue culture experiments. The effect of these "critical" and "subcritical" zones is quite a different concept than that of the usual low-temperature experiments in which tumor tissues as well as normal tissues have been subjected to actual freezing with carbon dioxide, liquid air and other agents without significant injury to the cells.

Parallel biopsy studies of the tumors treated locally at reduced temperatures revealed regularly regressive degenerative phenomena, resulting in some instances in the complete disappearance of the neoplastic process. The cytologic changes observed as affecting the tumor cells were in many respects comparable to those noted by irradiation therapy; *i.e.*, nuclear destruction and cytoplasmic disintegration. However, one striking difference was found between the two methods of treatment. Irradiation in effective therapeutic dosage shows little partiality and destroys normal tissue, including the smaller blood vessels, almost as regularly as it does the tumor cells. Thus, when healing occurs, a dense avascular cicatrix is likely to result. On the other hand, with reduced temperature alone—applied locally at 40 °F, for as long a period as five and a half months consecutively—no damage is done to the skin or supportive tissues. Indeed, repair follows as a normal regenerative process without true cicatrix formation. Ulcerative lesions of the breast, of the mouth and of those associated with fistulous development as seen in cervical carcinoma have been observed to heal completely.

One other important factor which we believe is concerned with this healing process should be mentioned. Temperature levels of 40-50 °F are pretty generally recognized as bacteriostatic for both the common saprophytes and the ordinary pathogens. As a result, in the absence of bacterial growth, the reparative reaction goes on normally, although at a somewhat slow rate. This, perhaps, explains the lack of dense scar formation. It likewise accounts probably for the loss of the foul-smelling, putrefactive character of the lesions, which has been noted almost regularly.

Following the initial studies of the effect of cold locally upon cancerous tissue, it was felt that if it were possible to reduce the entire body temperature to sub-critical temperatures of 85 to 90 °F, it might be possible to find similar regressive cell changes in metastatic foci. Accordingly, this was attempted clinically by Fay in a case of advanced carcinoma of the breast, who had an entirely hopeless prognosis because of widespread carcinomatosis. The original method of induction of this generalized low temperature has already been reported by us in an earlier communication.[4] Since that time, several modifications in technic have been adopted. At the present writing, the patient is given a small anesthetic dose of "evipal" to carry him through the period of discomfort while the temperature is falling from about 96 to 90 °F. Without this sedation there is a marked sensation of cold accompanied by severe shivering.

After the administration of the evipal the patient is moved to an air conditioned room maintained at a temperature of 58 °F and a humidity not exceeding 20 per cent. He is stripped, save for a loin cloth, placed in bed on a rubber sheet and his trunk packed with chopped ice. A rectal resistance thermometer is introduced and fastened in place with adhesive tape. This is attached to a constant recording apparatus (Micromax, Leeds Northrop Company), which accurately registers the temperature during a 24-hour period. A large clock-like dial which can be read easily across the room simplifies the maintenance of the constant temperature by the nurse, as the slightest variation can be detected instantly. Blankets or ice-bags are used as necessary to keep the temperature at the desired level once its induction has been obtained.

Arbitrarily, in bringing the patient's temperature down, when 90 °F is reached, which takes from one to two hours as a rule, the ice is removed and the patient's bed made up with dry linen. The temperature tends to fall the two or three additional desired degrees before it levels off.

Vaselined gauze is applied to the eyes to prevent corneal irritation, which is likely to occur because of the almost invariable suppression of tears. Recently, it has been routine practise to introduce a soft, rubber-tipped nasal tube into the stomach so that fluids and medication can be administered. Paraldehyde in small doses is used to control restlessness. This is given on a p.r.n. basis, cases who have previously been on large doses of narcotics requiring more than those who have not. As a result of initial studies on fluid balance it has been deemed advisable to give small amounts of saline with 10 per cent glucose at one- to two-hour intervals, totaling about 32 ounces in the 24 hours. No food is given, however, as this tends to activate metabolism with consequent temperature elevation. The routine duration of this generalized low body temperature is a four- or five-day period repeated at intervals of about a week for three or four times.

From December 1938 to October 1939, 33 patients have been subjected to 75 individual inductions of generalized reduced body temperature, ranging from 74 to 90 °F. All these patients have been hopeless, terminal cases of cancer, who have presented themselves chiefly for the relief of pain. They have had all the surgical and irradiation treatment indicated, and have been as a whole in extremely poor physical condition—emaciated, cachectic, often anemic. We emphasize these points because of their quite possible significance so far as comparative physiologic studies might be concerned in respect to normal, healthy, well-nourished individuals subjected to this same procedure.

We wish in this communication to record such physiologic data as we have obtained from a study of these patients while in this physical state, which resembles "hibernation" in many respects. An entirely new concept as it pertains to physiology has been opened up by these investigations, and an enormous amount of work will be necessary before any generalized conclusions can be justifiably drawn. The data which we wish to record are only fragmentary, and represent chiefly information which we needed from time to time to meet clinical problems as they arose. The effort to maintain constant temperatures in these lower ranges has been our primary object to date, so that we could critically evaluate in dosage so to speak, what the effect of the withdrawal of a given quantity of heat for a specified period of time would be, in respect to cell changes in the various types of tumors. It was early noted that disturbing the patient any more than was absolutely necessary invariably resulted in fluctuation in temperature. For that reason the more intensive study of the physiologic reactions was postponed until such time as the primary objective, namely the effect of cold on the actual cell structure, could be measured quantitatively.

Blood

Based on Huggins and Noonan's observations of the bone marrow in white rats as affected by alteration in temperature, considerable concern was felt regarding the possibility of the development of an anemia in these patients. It seems logical to assume that the precursors of the fully maturated cells of the peripheral circulation might well be considered as "embryonal" in character. As such, it further seems logical to expect some alteration or repression in their maturation pattern. In addition, it must be borne in mind that a variable degree of anemia already existed in the majority of the cases as a result of their disease. This may have to be taken into consideration in analyzing the data finally.

Also, possible alteration in blood volume and rate of flow, as well as blood-pressure changes, may represent complicating factors which will acquire statistical significance in the final computation. Recognizing fully these possible criticisms, it still seems worth while to record what can be considered scarcely more than preliminary impressions in this regard. In the earlier series of cases, using Avertin, barbiturates and withholding all food and fluid, no very striking changes were observed in the actual red count. Indeed, at times the count appeared to rise slightly, but at the same time there was a tendency for the hemoglobin, as expressed in actual grams, to fall slightly. This was felt to represent a hemoconcentration as a result of disturbance of the fluid balance. Accordingly, the later series of cases have had their fluid balance maintained by the administration of small amounts of saline by nasal tube.

It appears that the development of an actual anemia is one of the complications which must be guarded against. This is not usually apparent in the first, or even the second period of generalized refrigeration, but tends to appear in the further induction periods. An instance in which a drop in the hemoglobin from 10.5 to 7 grams occurred has been recorded. In the majority of cases, the development of the anemia has been very slight with at the most a drop of 0.5 to 1.0 gram over a period representing a month to six weeks. The actual red counts have roughly paralleled these hemoglobin changes, but in general have not been as impressive, the total cell change rarely exceeding half a million.

When we turn to a consideration of the white cells, however, almost regularly a very striking leukocytosis has been observed. This frequently takes place within the first 24 to 48 hours of the period of reduced body temperature. Counts as high as 50,000 white cells have been recorded. The usual rise observed is to a level somewhere between 15 and 20 thousand. In several of the cases, a minimal rise has been observed of not more than two to three thousand cells. This has been particularly true in those cases in which an anemia already existed before the patient's temperature was reduced. The differential count in these cases shows very little variation from normal with perhaps a slight emphasis on the neutrophilic side, the majority of the cases showing a leukocyte percentage ranging from 60 to 75. Occasionally, a very striking, predominantly neutrophilic picture has been seen, in one instance at least, averaging 93 per cent during the course of four inductions with the total white count ranging from 14,850 to 44,800. These elevated counts drop promptly within 24 to 48 hours after the temperature returns to normal. At this time we have no adequate explanation to offer for this phenomenon.

Preliminary circulation time studies made through the coöperation of Dr. M. J. Oppenheimer of the department of physiology suggest that the circulation rate is nearly halved in the peripheral vessels. It is suggested that such slowing of the circulation might result in the accumulation of the white cells in the smaller vessels. Possibly because of the lower temperatures, there is actually an increased viscosity of the blood. These are suggestions which will require further study to corroborate.

Renal Function

In analyzing the scattered blood chemistry determinations which we have obtained during the course of observation of these patients, again there is a division into the earlier series where prolonged anesthesia with avertin and barbiturates was employed, and into the later series where evipal and paraldehyde have been used. One of the basic differences between these two groups has further been in the maintenance of fluid balance in the later cases. In the early group, renal function seemed to be entirely at a standstill. In the later group, fluid balance has been established, the kidneys excreting within two to three ounces of the amount of fluid administered. The majority of these cases have received on an average from 30 to 34 ounces of saline and have shown an output of from 26 to 32 ounces. Thus, it seems quite obvious that the kidney is capable of function, dependent upon the load put upon it. Even a damaged kidney in a case in which there were symptoms of impending uremia has shown this functional capacity, with resulting decrease in the urea content of the blood during the period of reduced temperature.

Urinalysis in all these cases has shown nothing of pathological significance from the routine examination. No red cells or casts have been observed in any of the cases, and in the few instances in which more careful analytical studies have been made chemically, no excess of any of the usual constituents has been observed either during the period of refrigeration, or following it. In this connection, autopsy studies upon cases ultimately dying of their disease have shown no evidence of damage to the glomeruli or tubules, as was feared might result from such exposure to cold.

Blood Chemistry

Closely related to these observations upon renal function must be considered the blood chemistry data. As has already been stated, only scattered observations have been made, as venipuncture has been avoided as far as possible in order not to arouse the patients and cause alteration in their temperature. However, there are 59 individual urea nitrogen determinations, 31 blood-chloride determinations, 54 blood-sugar determinations, and 41 carbon-dioxide observations with scattered additional observations on calcium, phosphorus, cholesterin, non-protein nitrogen and creatinine, as well as total protein, albumin and globulin. In going over this data, certain features stand out prominently. Even in the early cases where no fluid was given and renal function was at a minimum, no evidence of nitrogen retention was found. Indeed, not infrequently a slight drop in the average figure was found. In the latter series of cases where fluid balance has been maintained, this drop in urea has been even more pronounced. It has not been uncommon to find readings as low as four milligrams and the usual reading has been somewhere in the vicinity of ten milligrams. In some instances where the urea has been somewhat elevated before temperature reduction has been attempted, this drop has been less striking but has occurred with surprising regularity.

Before the introduction of saline to maintain fluid balance, a reduction in chlorides had been observed. This has been corrected by the modified procedure.

Blood sugar, likewise, has shown a tendency to drop to the lower levels of normal, the average figure ranging somewhere between 80 and 90. Occasional readings as low as 60 milligrams have been seen. In many instances, however, no significant drop has been observed, and levels between 110 and 120 have been maintained. No instance of a diabetic patient has been encountered. Because of this slight drop in blood sugar, however, the glucose commented upon earlier in the paper has been added to the saline with the maintenance of more nearly normal levels in blood sugar.

Again, in the early cases, there was a slight tendency for the carbon-dioxide picture to rise, but with the maintenance of fluid balance, these figures have all remained within normal levels. No significant alteration in any of the other factors has been observed.

Basal Metabolic Rate

In the original report by Smith and Fay,[4] the effect upon the respiration of these patients was noted. The rate tends to be somewhat irregular and the breathing shallow. Many of the patients show very little variation in actual rate, but others may show a drop to as low as ten or twelve, while still others may show an elevation to as high as 28 or 30. For this reason the recording of basal metabolic rates by the usual indirect method has been somewhat unsatisfactory and perhaps not entirely reliable. However, it is our impression from the 51 determinations which have been made that there is an actual reduction in basal metabolism during the period of reduced temperature. This reduction has varied from as little as 6 to as much as 25%. It is doubtful if these represent the actual reduction in metabolism which appears to be existent. From all the other laboratory and clinical observations, we suspect that the only way to get accurate metabolic rates will be by direct calorimetry, as in at least two cases with generalized reduced temperature, we have seen a sharp elevation in the metabolic rate as recorded by the ordinary Jones Basal Metabolic Apparatus as compared with their pre-observational period. This was apparently the result of a very erratic and rapid shallow respiration.

Comment and Discussion

In reviewing the physiological data which have been recorded, both as clinical observations in respect to the patient's circulatory apparatus and respiratory system, and from laboratory studies, it becomes apparent that an entirely new field in human physiology has been opened for investigation. Previous to these studies, so far as we have been able to determine in a careful review of the literature, no comparable observations on human beings have been recorded. Indeed, it has been the general impression that any prolonged reduction of temperature below 94 or 95 °F was inevitably fatal. These studies have brought out the fact that patients can be maintained for periods as long as five to eight days at temperature levels in the eighties; that relief of pain can be regularly anticipated for periods of time ranging from a few days to as long as five months, and that regressive changes in young embryonal cells, particularly in carcinomata, take place as a result, we believe, of lowered physiological activity, interfering with the metabolism of these cells. These preliminary studies upon the physiological mechanism involved suggest that the entire body economy is reduced, that the circulatory rate and blood flow are slowed, and that the liver is in a relatively dormant and inactive state as shown by the low nitrogenous analyses of the blood. Basal metabolism is apparently reduced by as much, perhaps, as 20 to 25 per cent; and even lower figures may well be anticipated when special methods are devised for the more accurate recording of these observations. Just how far these alterations in physiology may prove of clinical value in medicine remains an entirely open question. Thus far, we have observed what we feel to be beneficial effects in cases of malignancy, in cases of drug addiction and in a single instance of psychiatric derangement. No doubt exists in our minds that the procedure is one comparable in many respects to other major therapeutic methods and is not entirely devoid of risk. It is a method which should certainly only be attempted by individuals or groups where opportunity for careful observation of the patients can be made available. One thing stands out as a clear-cut result of these studies: the use of low temperatures in the control of pain. This is perhaps more particularly applicable from the clinical standpoint to chronic cases, especially to the terminal stages of cancer where patients are bedridden and such measures are more readily employed. Its usefulness in the therapeutic field otherwise remains a problem to be solved in the future.

Discussion

J. D. Hardy: Aside from the important clinical applications of this brilliant piece of work there is the unexplored physiology of the hibernating state applied to warm-blooded animals. This work will probably occupy many of us for years and it is fitting that this pioneer effort should be presented at this symposium. I should like to inquire of Drs. Smith and Fay what, if any, neurological effects were observed in patients immediately following their return from the hibernating state? Also, does the amount of temperature drop or the duration at a specific level seem to be generally the most important factor in changes caused during the hibernating state?

H. C. Bazett: There is little I can add to the discussion. I would merely like to take the opportunity of expressing my great interest in this new field. The physiological problems are many and complicated. Among these one would like to know what R Q is found for metabolism at these low levels. Data on poikilotherms suggest that there are considerable changes in R. Q., though mainly during the period of readjustment. The authors deserve congratulations for their pioneering work.

Reply

Temple Fay: In answer to Dr. Hardy, variable mental responses have been noted upon return of the patients from the state of refrigeration. This I believe depends upon the type and amount of sedation employed. Originally we were anxious to spare the patient any discomfort or recollection of the application of cold, so that at first I adopted the routine in use in my clinic for neurosurgical procedures on the brain, namely, 20 g of sodium bromide and 10 g of chloral hydrate, by mouth, the night before and the morning of induction. Avertin, (50 mg per kg of body weight by rectum) at the desired time, brings about prompt anesthesia which is then sustained for 2 to 3 hours. Amyelene hydrate and barbiturates were given later to maintain sedation of anesthesia.

One can readily see that neurological responses could hardly be properly evaluated under such sedation; nevertheless, we found it necessary to maintain the patient in a *non-active* state, in order to obtain a satisfactory reduction in body temperature. Activity or feeding tends to raise body temperature.

The use of ice-packs or a refrigerated water-cooled blanket, for the purpose of quickly reducing temperatures, has been found to be satisfactory. The rapidity of fall in temperature depends also upon the amount of fatty tissue present: thin patients are quickly and easily induced.

In most instances a "shivering reaction" occurs as the rectal temperature approaches 97 °F and is sustained until it reaches below 93 °F. As the effect of the Avertin lasts only about three hours, an attempt to reach 90 °F or below, within this period is most desirable. Dr. McCravey (Neurosurgical Fellow) and I have found, however, that repeated fortification of sedation with amylene hydrate gave evidence of cumulative toxic effects upon recovery from the hibernation. Certainly some of the early observations or anuria and absence of blood-pressure can be definitely ascribed to the degree of sedation. Post-refrigeration states of mental torpor, and "groggy" phases must also be ascribed partly to this factor.

In two instances, definite signs of "wet brain" occurred, which led us to abandon amylene hydrate and the barbiturates, replacing these with a 20 per cent paraldehyde solution in acacia, by mouth. Cerebral edema has not been noted since discontinuing the barbiturates.

During the past six months we have used less and less sedation during the process of refrigeration because the patients have had no recollection of events during this period, even though they have been maintained for as long as eight days, with rectal temperatures below 90 °F and in a conscious state, able to talk, respond, eat and coöperate.

The speech and mental processes are distinctly slowed under refrigeration and there is a state of dullness manifested on the part of the patient during the first 24 hours after recovery. This is followed by a period of return of appetite and increased interest and alertness.

It must be remembered that these individuals are not normal, but represent the final stages of hopeless cancer. The relief of pain which refrigeration brings to these people is remarkable. Release from suffering and need of narcotics may be partly responsible for the improved mental state.

This brings me to a point that will interest Dr. Hardy. In every instance where sustained cold has been applied locally or in the form of generalized refrigeration for 24 hours or more, pain has been relieved for days or even months. I have attributed this prompt response to devascularization or release of "stretch" on the pain fibers by the tumor shrinkage. Dr. Hardy, I understand, feels there is a more profound physiological reason for the relief of pain following the application of cold.

There are a great many physiological questions which immediately arise in this new field and under conditions which have not been observed before. I have attempted to maintain certain temperatures locally or generally, for varying periods of time, so that I could furnish Dr. Smith with biopsy material for comparative studies.

Arousing the patient for tests has been avoided because it has often been followed by restlessness and a rise of temperature, requiring added efforts to quiet the individual, in order to stabilize the temperature record again.

Our observations in this paper have been concerned with the effects of reduced temperatures on undifferentiated cell activity, which Dr. Smith has so carefully recorded.

Finally, I wish to assure you that exploring this new field of refrigeration has not been without its anxieties, because of the utter lack of precedent; and although I have seen a rectal temperature in the human sustained at 75 °F, and nearly 100 instances where it has been maintained for days below 90 °F, I still experience the same apprehension each time I undertake the procedure that I did, just one year ago, when I took the first patient down to 91 °F.

I was taught by our Chairman, Dr. Bazett, and others, when a student at the University of Pennsylvania, that human beings could not long survive at temperatures below 95 °F. Since Dr. Bazett is partly responsible for this unpleasant reaction and fear which I still have, I am delighted to give back to him and to the other physiologists in general, something for them to worry about. I am certain a host of new problems exist in this wide field of at least 20 °F below anything they have contemplated, so far as the human species is concerned. Thank you.

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Chapter 7

Automatic Temperature Regulation and Recording

Elementary Theory of Automatic Temperature Regulation (Control)

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The subject of automatic temperature regulation is in great need of elucidation and simplification at the present time, because the many papers and discussions which have appeared in recent years have approached it from angles which leave it obscure to the new student and busy engineer. Some papers have been wholly descriptive and others mathematically abstract. The literature on the subject is apparently voluminous for it is an old field of applied physics which is entered occasionally by engineers and others from many other fields. Often these entrances are followed by the publication of notes describing the device which was invented during the visit. One author recently stated that "little has been published relative to the fundamental principles," and another "the science of the automatic regulation of temperature is at present in the anomalous position of having erected a vast practical edifice on negligible theoretical foundations." The theoretical foundations are so old that they have merged into the landscape and the fundamental principles found in classical texts on the sciences have not sifted into the field in generally recognizable and useful form. The young engineer can learn only with difficulty about the elementary theory from the available descriptive essays and ordinarily inaccessible patent specifications, and, so far as we are aware, no analytical approach to the subject has been published which could be generally useful. Ivanoff's[1] excellent essay in which he used one of Fourier's heat conduction equations in disguised form proved, at least, that too rapid mathematical excursions are likely to lead to erroneous generalities, and the discussion which followed his presentation demonstrated the futility of his method of approach. Since the expression of ideas in mathematical language is the essence of applied science and engineering, it is essential that the principles of this subject be expressed in mathematical form, but it also is essential that mathematical flourishes be avoided.

It is particularly desirable to begin the study of this subject with the simplest mathematical expressions, because the theories of heat transfer are more difficult to grasp than, for example, those of flow ordinarily involved in the regulation of the level of a liquid. We will find it necessary presently to confine our treatment strictly to the regulation of temperature as a problem essentially different from the regulation of anything else, and we are inclined to disagree with those authors who are currently attempting to teach the subject with the use of hydraulic analogies, and who imply that a study of level control is a good approach to that of temperature control. For example, Mason[2] suggests that a study of control of the level of a liquid in the continuous process may be universally applicable in the study of automatic regulation, including temperature, failing to note that the analogy converts to temperature control, not of the continuous, but of the batch process; he also fails to distinguish between the two processes. The conversion results from the substitution of the flow of heat for the flow of a liquid. For a study of the thermal processing of liquids where the heat is transferred principally by convection, there are available theories based on the analogies of fluid flow and heat transfer,[12] but it would seem advisable to handle the problems of conduction and radiation in a conventional manner.

The first principles of automatic control are best derived from a study of so-called throttling control, in which the heat supply is maintained at some intermediate value, for example, by a partially open valve. A better name for this method of control would perhaps be corresponding[8] control, because for every temperature within the throttling zone of the controller there is a corresponding position of the valve. It seems that in spite of the fact that volumes have been written and hundreds of patents issued on this method of control, there remains unavailable, so far as the writer is aware, any simple exposition of the fundamental concepts which should be identified with it. Most writers are prone to plunge into the general subject with vague expression of the first principles, or omission of reference to them as too elementary to consider, while most inventors pay little attention to the fully developed theories of heat transfer and damped periodic motion, confining their attention for the most part to the invention of various means for "beating" physical laws.

Probably the *first principle* of control is that the controller combats, or corrects for, a change in temperature; that is, if the temperature departs from the selected control point, the controller acts to restore it.

The *second principle* depends on the fact that temperature is always controlled indirectly, generally by controlling the rate of supply of heat according to the variations in temperature, thus leaving the load or heat demand an independent variable. Hence, the result of controller action depends not only on the characteristics of the controller, but on those of the plant being controlled, including independent variations in load.

The *third principle* is (in corresponding control) that a permanent change in demand for heat can be corrected only partially, and only with an accompanying permanent change in temperature in the opposite sense. Thus, if the demand

Table 1. Definitions of Symbols.

A = area, variable; A_e = area, constant
α = thermal diffusivity
c = specific heat
k = conductivity only in $\alpha = \frac{k}{c\rho}$
L = thermal load, *e.g.*, lbs per second times average specific heat
λ = wave-length
ln = abbreviation for $\log_e$
n, k, k_1, etc., a, constants
p = pressure, variable; p_e = pressure, constant
Q = volume rate of flow
q = heat input, *e.g.*, watts, or B.t.u. per second
q_m = amplitude of q
R = resistance to flow
ρ = density
s = sensitivity (see text)
s' = apparent sensitivity
t = time
T = period of oscillation in seconds
θ = temperature or small departure from a fixed value
θ_0 = θ at $x = 0$; also, reference temperature
θ_m = amplitude of θ_0
θ_L = θ at $x = x_L$
θ'_m = amplitude of θ_l
v = velocity
V = volume
x = variable distance

decreases, the temperature remains higher than the selected control point in order that the heat input may be maintained at a lower rate. This departure of the temperature from the control point may be called the "load error." A similar departure may result also from a permanent change in the potential of heat supply, for example, the pressure of fuel gas or the voltage of electric supply, but in this case the error is in the same sense as the change in potential.

While the load error can be kept small by designing this controller so that its corrective action is relatively very large, the error will remain real, although it may be reduced to a negligible value.

The idea of the characteristic of sensitivity is very old, and it has long been recognized that as the throttling zone of a controller is narrowed; that is, for example, a valve is made to move to its limits for a smaller range of variations in temperature, the controller appears to be more sensitive and corrects the better for changes in temperature, to the point where it may be so sensitive that it imposes maintained oscillations upon the plant—it is said to "hunt." It is essential then to be able to define sensitivity with some degree of exactness.

The Steady State

With these elementary principles in mind, we shall first study the steady state of heat transfer.

Suppose that in a plant having a corresponding controller attached to it, the temperature is temporarily remaining constant because the demand and supply are at the moment both steady. Let us move the indicator or measuring element of the controller an infinitesimal amount $d\theta$, thus changing the heat input an amount dq, and hold the element forcibly by hand in this new position until the temperature has become steady at a new value. Now if the element is suddenly released it will move in the opposite direction from the way we were holding it to a position differing from the original one by an amount $-(d\theta)_a$, the minus sign indicating the primary function of the controller to combat a change. The relation between $d\theta$ and $(d\theta)_a$ is simply

$$(d\theta)_a = -s\,d\theta \tag{1}$$

where s is a constant of proportionality.

The change $(d\theta)_a$* resulted from a change, dq, in the heat input. Now, if s is to be truly a constant, *i.e.*, Equation (1) is to hold for all values of load and positions of the controller, then the controller must be so designed that dq will vary according to the relation between q and θ in the uncontrolled plant, (uncontrolled because during the test just described the controller is prevented (held) from functioning). In the continuous process, assuming that the heat lost is small compared with the total required, the temperature of the uncontrolled plant varies according to the equation:

$$q = L(\theta - \theta_0) \tag{2}$$

where θ_0 is a reference temperature.

At any constant value of L at which the holding test is made:

$$dq = L(d\theta)_a \tag{3}$$

and from (1):

$$dq = -Ls\,d\theta \tag{4}$$

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* This is the same as Ivanoff's "potential temperature."

Dividing Equation (4) by Equation (2) eliminates the variable L, and we get:

$$\frac{dq}{q} = \frac{-s\,d\theta}{\theta - \theta_0} \tag{5}$$

and integrating:

$$k \tag{6}$$

This equation may be called the static equation of a controller designed to have the constant sensitivity s when applied to control a continuous process. It states that the heat input is *corrected* proportionally to the s power of the temperature, or, referring to the differential form, Equation (5), a fractional change in temperature under constant load results in a fractional change in heat input of s times as much in the opposite sense. Note that both sides of Equation (5) are dimensionless, and that s in these equations is revealed as the sensitivity of the controller in a commonly accepted meaning of sensitivity.

A simple equation in θ, L showing how the temperature of the controlled plant varies with L, is obtained by combining Equations (2) and (6):

$$(\theta - \theta_0)^{s+1} = \frac{k_2}{L} \tag{7}$$

Differentiating, and dividing by Equation (7):

$$\frac{d\theta}{\theta - \theta_0} = \frac{-1}{s+1}\,\frac{dL}{L} \tag{8}$$

This equation states that the fractional change in temperature, or load error $d\theta/(\theta - \theta_0)$, or simply $d\theta/\theta$, where θ is large compared to θ_0, of a corresponding controller of sensitivity s controlling a continuous process, is $1/(s+1)$ times the opposite fractional change dL/L in the load. For example, if s is equal to 19, a 20 per cent change in load results in a one per cent change in temperature. Equation (8) in this dimensionless form will be found to be very useful, for the assumptions made in the simple derivation are not very restrictive.

The so-called batch process may be regarded in the present state of theoretical development as one in which the heat input is equal to the heat lost, this loss being a function of temperature. We shall select the case in which heat is being supplied in fuel form from an uncontrolled supply pressure, p, through a valve having a controllable variable opening, A, and assume that the heat supply is proportional to Ap, as a sufficient approximation. We might have selected, on the other hand, electric heating with controllable current at an uncontrolled voltage. For the present purpose it will be sufficient to write, without violent assumptions, that

$$A_o p = k_3 \theta^n \tag{9}$$

for the equation of the uncontrolled plant; that is, the position of the control valve remains at that corresponding to a constant opening, of area A_o, and the heat supply is $q = A_o p$. In Equation (9), n is a constant usually less than 2. Suppose, however, that we propose to manipulate the controller by hand as we did to demonstrate the action of the controller on the continuous process, thus altering A while p remains constant at p_c. Then for the equation of the "manipulated" plant we have

$$A p_o = k_3 \theta^n \tag{9'}$$

While the temperature of the plant is for the moment, steady, let us move the indicator or measuring element an infinitesimal amount, $d\theta$, thus changing the heat input an amount proportional to $p_o dA$, and hold the element forcibly by hand in this new position until the temperature has become steady at a new value. As before, when the element is released it will move to a position differing from the original one by an amount $-(d\theta)_a$. The relation between $d\theta$ and $(d\theta)_a$ could be represented by Equation (1), but in this case the thermal load, which is equal to the heat lost, has changed with the temperature, and we shall write the relation

$$(d\theta)_a = -s'd\theta \tag{10}$$

where, comparing it with Equation (1), s' is the apparent sensitivity. From (9′):

$$p_c dA = k_3 n\theta^{n-1}(d\theta)_a \tag{11}$$

and from (10):

$$p_c dA = -k_3 ns'\theta^{n-1}d\theta \tag{11'}$$

and from (9′):

$$\frac{dA}{A} = \frac{-ns'd\theta}{\theta} \tag{12}$$

and integrating:

$$\theta^{ns'} = \frac{k_4}{A} \tag{13}$$

or putting $ns' = s$:

$$\theta^{s} = \frac{k_4}{A} \tag{14}$$

Equation (13) may be called the static equation of a corresponding controller designed to have the constant sensitivity $ns' = s$ when applied to control a batch process. It states that the heat input is corrected proportionately to the ns' power of the temperature, or, referring to Equation (12), a fractional change in temperature results in a fractional change of heat input of ns' times as much, in the opposite sense.

Referring again to Equations (9) and (9′), we may write

$$Ap = k_3\theta^{n} \tag{15}$$

for the equation of the controlled plant where, from Equation (13):

$$A = \frac{k_4}{\theta^{ns'}} \tag{16}$$

or, combining (15) and (16)

$$\frac{k_4 p}{\theta^{ns'}} = k_3\theta^{n}, \tag{17}$$

or

$$\theta^{ns'+n} = k_5 p \tag{18}$$

and

$$\frac{d\theta}{\theta} = \frac{1}{ns'+n}\cdot\frac{dp}{p} = \frac{1}{s+n}\cdot\frac{dp}{p} \tag{19}$$

The effects of self-regulation[4] are seen in the factor $s+n$ of Equation (19) in place of $s+1$ in Equation (8), and the factor s', equal to s/n in Equation (10) in place of s in Equation (1). The expression "self-regulation" is used to describe the retarding effect of the change in heat lost that accompanies a change in temperature. For example, if the pressure of fuel supply to an uncontrolled batch process rises, the temperature will rise, but this will result in an increase in heat lost, which will in turn tend to prevent the rise in temperature. The effect is negligible in the continuous process.

Equation (19) [cf. Equation (8)] states that the fractional change in temperature, or heat-potential error, $d\theta/\theta$, of a corresponding controller of sensitivity, s, applied to a batch process is $1/(s+n)$ times the fractional change, dp/p, in the heat potential. The equation, likewise Equations (12) and (13), will be used cautiously for drawing conclusions.

Before passing on to a study of the varying state, we would like to make a few observations that may be of interest to those readers who are familiar with the general subject, and in particular, those who have been following the contributions by the A. S. M. E. Committee on Industrial Instruments and Regulators. A static equation of a "corresponding" regulator including s, the sensitivity, as a constant must take a form similar to Equation (6) for the continuous process. That is, it must be built up after eliminating the expression for the load; otherwise s will not be constant, but will vary with load or demand. Not only does the choice of these equations offer a more readily understandable starting point in a study of temperature control, but, so far as we know, they have made it possible for the first time to derive simple expressions for load error. These expressions are simple, because fundamentally an expression for load error can be simple only if based on an equation in which s is truly a constant. Thus if s varies with load, then an expression for the load error will involve load as a variable; and the simplest expression must be limited to a specified load, or, what is the same thing, a specified position of the regulator in regard to the limits of the throttling zone, *e.g.*, half-way between the limits.[5] However, we do not propose to use the foregoing equations for a study of dynamic conditions, because their combination with harmonic functions would lead to cumbersome forms.

The Varying State

Our first consideration in beginning a study of the dynamic characteristics of a controller or its combination with the plant is to select conditions which will teach us the most in the simplest way. Some authors begin with the selection of a standard disturbance. There are a number of objections to this method of approach. (1) The mathematics is needlessly complicated, no matter what form is assigned to the disturbance. (2) Temperature waves from the heat source to the thermometer travel so very slowly that there are no inertia effects of appreciable magnitude, in the controller or any of its parts, that must be studied in order to learn how the controller will respond to the disturbance. (3) Theoretically, it may be considered as a fault in design if a controller does not respond to a disturbance properly when it is adjusted as to sensitivity and damping at the preferred values. For example, excessive damping may be required to counteract the deleterious effect of an excessive dead zone, making it necessary to release the damping when a strong disturbance arises. Let us begin, then, with the oscillating condition.*

A *fourth* very simple *principle* of automatic temperature control is that oscillation, or hunting, will persist only if each successive wave of temperature reaching the thermometer is at least as large as its predecessor, and if successive waves decrease they will die out, and there will be found a damping force somewhere in the system. The combination of controller and plant may be regarded as two oscillating units centered at the valve and the thermometer, like two swinging pendulums joined with a spring and a dashpot, although the likeness is very remote and we will not be concerned with it further.[6]

Referring to Fig. 1, suppose that water to be heated is flowing at constant velocity in the pipe from valve to thermometer, that heat enters at the valve, and that the position of the valve is made to correspond to the temperature of the thermometer by means of a "follow-up" linking the two. We shall assume for the moment that there is no lag of the thermometer, no damping device in the follow-up (the valve moves in instant response to the thermometer), and no heat lost from the water between the valve and the thermometer. If now we find the controller hunting, then [cf. Equation (6)], when the thermometer is at its highest point of swing corresponding to the crest of a temperature wave, the valve is at its smallest opening corresponding to the trough of the wave, and a sensitivity of unity is just sufficient to maintain hunting. Such a sensitivity maintains each successive wave at a constant amplitude, according to the definition of sensitivity. Our controller now has the very poor characteristic of large load error, in fact equal to $\frac{1}{2}$ the change in load [Equation (8)], and hence the sensitivity must not be reduced to stop hunting. On the other hand, the sensitivity should be increased while some other means is found to stop hunting. There are unavoidable damping forces in any real case, such as attenuation of the temperature wave as it passes through the wall of the thermometer inclosure, accompanied in this case, unfortunately by delay in response of the thermometer. However, this single effect may permit the use of sensitivities well above unity for the continuous processes. Still higher sensitivities are made possible through the use of various damping devices at the valve or in the follow-up system. Any of these should avoid, of course, the imposition of any time delay in excess of that corresponding to the damping action.

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* Ivanoff used a square wave as his standard disturbance, represented by a Fourier's series, and did not use a harmonic oscillation for the standard, as stated in a recent contribution to the A.S.M.E. committee mentioned above, but he did begin with the oscillating condition.

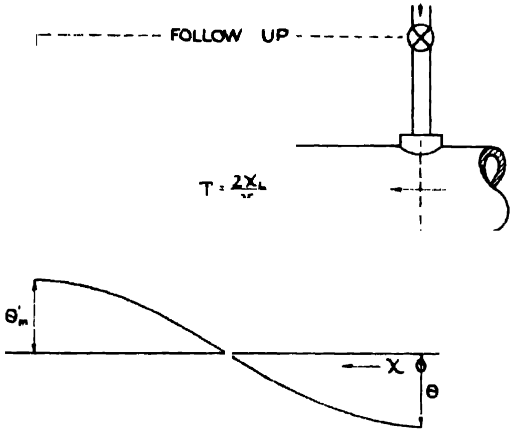

FIG. 1. Corresponding control of the continuous process. Undamped temperature wave. Equation (20) et seq.

Referring again to Fig. 1, and assuming as before that there is no lag at the thermometer, no heat lost between the valve and the thermometer, and no damping device is used in the "follow-up," sustained temperature waves starting at the valve and passing the thermometer can be represented by the well known equation:

$$\theta = \theta_m \cos 2\pi \,(t/T - x/\lambda), \tag{20}$$

in which θ is the departure of the temperature from a mixed value. This equation defines θ for all values of t and x, a stationary wave being defined for any time, t_1, and the oscillations about any point x_1. Putting $\theta=\theta_0$ in the plane $x=0$:

$$\theta_0 = \theta_m \cos\,(2\pi t/T) \tag{21}$$

For small variations $s\theta_L = -\theta_0$, and if $s=1$,

$$\theta_L = -\theta_m \cos(2\pi t/T) = \theta_m \cos(2\pi t/T - \pi) \tag{22}$$

where θ_L is now the value of θ in the plane $x=L$.
From (20), putting $x=x_L$, and (22),

$$2\pi x_L/\lambda = \pi \text{ and } x_L = \lambda/2 \tag{23}$$

The thermometer is one-half wave-length from the valve. The velocity of the wave is $v=\lambda/T=2x_L/T$. $T=2x_L/v$.

It is apparent without proof that the velocity of the temperature wave is the same as the velocity of the stream of liquid, and that in this case the period T is twice the time lag x_L/v.

If s is less than 1, then each successive wave is smaller than the preceding one, and the train of damped waves is represented by

$$\theta = \theta_m e^{\overline{\ \lambda\ }} \cos 2\pi(t/T - x/\lambda), \tag{24}$$

where $\lambda = 2x_L$ as before.

$$\theta_m \tag{25}$$

The so-called logarithmic decrement, or log of the ratio of succeeding crests (a full wave-length apart), is

$$k = 2 \ln s \tag{26}$$

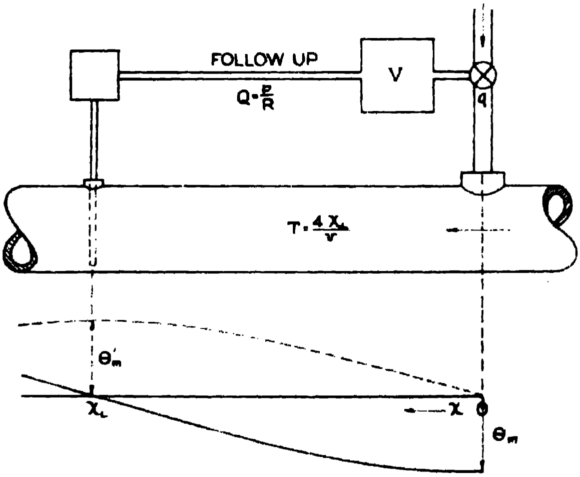

Fig. 2. Corresponding control of the continuous process. Undamped temperature wave. Damped Regulator. Equation (27) et seq.

Referring now to Fig. 2, let us suppose that there is interposed between the thermometer and the valve a damping device, consisting of a compressed air line and tank, the line having a resistance to flow. For our present purpose we may write,

$$Q = p/R, \tag{27}$$

where Q is volume rate of flow of air in the connecting line, resulting from a departure, p, in pressure from a fixed value, and R is the resistance to flow. Also, for small departures, as before,

$$-s\theta_L = p \tag{28}$$

taking the constant of proportionality as unity.

If the position of the valve is determined by the pressure in the tank, then,

$$\frac{dq}{dt} = \frac{Q}{V} = \frac{-s\theta_L}{RV} = \frac{-s\theta'_m}{RV}\cos 2\pi(t/T - x_L/\lambda) \tag{29}$$

$$q = -\int\frac{s\theta_L}{RV}\,dt = \frac{sT\theta'_m}{2\pi RV}\sin 2\pi(t/T - x_L/\lambda) \tag{30}$$

$$= \frac{sT\theta'_m}{2\pi RV}\cos\left[2\pi(t/T - x_L/\lambda) + \pi/2\right]$$

$$= L_1\theta_0 = L_1\theta_m\cos(2\pi t/T)$$

Then

$$\frac{2\pi x_L}{\lambda} = \frac{\pi}{2},\quad x_L = \lambda/4, \text{ and} \tag{31}$$

$$\frac{\theta_m}{\theta'_m} = \frac{sT}{2\pi L_1 RV'} \tag{32}$$

the ratio of the amplitude at $x = 0$, to that at $x = x_L$

The equation of the damped wave is:

$$' = \theta_m e^{\overline{\ \lambda}}\cos 2\pi(t/T - x/\lambda), \tag{33}$$

and from (31) and (32)

$$e^{\frac{-k}{4}} = \frac{sT}{2\pi L_1 RV} \tag{34}$$

In this case the period $T=4x_L/v$, or four times the time lag, whatever the degree of damping determined by the sensitivity s, the capacity V of the tank, and the resistance R to flow of air, provided that the damping is small enough to permit decaying oscillations following a disturbance. For example, relatively rapid recovery will result if the first overswing is 10 per cent of the departure, and the second or return overswing is 1 per cent. Commercial controllers are equipped with means for adjusting sensitivity and damping, and for this reason extension of the analysis beyond this point is of interest mainly to the instrument designer. General interest lies in the observation that damping permits the use of high sensitivity, which results in small errors caused by changes in load.

Delayed response accompanies damping of a controller; hence we come to a *fifth principle*, that high sensitivity made possible for the continuous process by damping the controller is incompatible *per se* with quick response of the controller to a disturbance. It is possible, of course, to incorporate in the controller a damping release which functions when a selected value of the rate of disturbance is exceeded. Such a device will result in overshooting the control point by a large amount following the first return from the disturbance, and under very unsteady conditions to be controlled the releasing device may function so frequently that no effective damping remains.

The time lag met with in the continuous processes, as illustrated in Fig. 1, unaccompanied by any attenuation of the temperature wave, presents one of the more difficult problems in temperature control. However, before discussing the case of the continuous process further, we shall proceed to the consideration of the case of temperature attenuation met in heat conduction, particularly in the heat treatment of solid charges such as the annealing of metals and alloys. The first principles are learned from the study of heat conduction through solids, the simplest case of this being linear flow of heat.

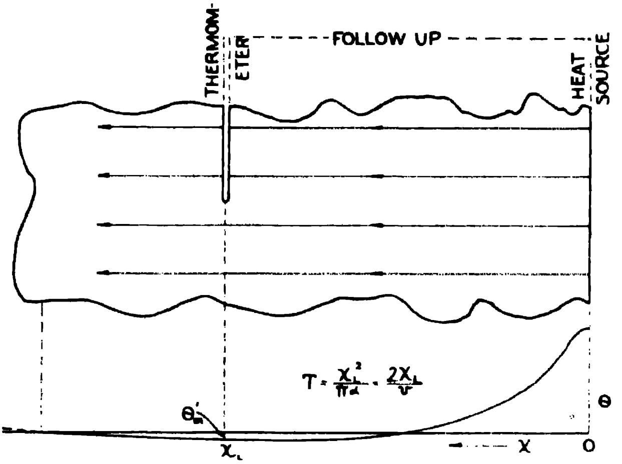

FIG. 3. Corresponding control with attenuation of temperature. Damped temperature wave. Equation (35) et seq.

Again let us suppose that the controller is hunting, that is, maintaining a train of temperature waves travelling from the heat source to the thermometer. Referring to Fig. 3, the thermometer within the solid conductor is connected by an undamped follow-up device to the heat source covering the plane face. An experimental approximation to this arrangement furnishes the observation that the variation of temperature of the heated face closely follows a simple harmonic function of time, and the train of waves traversing the solid may be represented by the classical equation, in the most convenient form we have found:[12,13]

$$\theta = \theta_m e^{-x\sqrt{\frac{\pi}{\alpha T}}} \cdot \left(\frac{2\pi t}{T} - x\sqrt{\frac{\pi}{\alpha T}}\right), \tag{35}$$

where α is thermal diffusivity. If there is no lag of the thermometer at distance x_L from the source and no delay in the "follow-up" then, as before, for the corresponding controller,

$$x_L : : \lambda/2 = \sqrt{\pi\alpha T} \tag{36}$$

by comparison of Equation (35) with Equation (20) or (24).
The amplitude at $x = 0$ is θ_m, and at $x_L = \lambda/2$ is

$$\theta'_m = \theta_m e^{\frac{-\lambda}{2}\sqrt{\frac{\pi}{\alpha T}}} = \theta_m e^{-\pi} \tag{37}$$

The ratio of θ'_m to θ_m is $e^{-\pi}$, that is, the wave is attenuated at the thermometer to 1/23.1 of its amplitude at the source; hence in this case an undamped controller must have a sensitivity of 23.1 to be able to maintain the oscillations. In a real case, the thermal capacity of the heating element will introduce further powerful damping, and with a controller of negligible dead zone, sensitivities of over 100 are required to maintain hunting. Further study of these equations leads to interesting results. The time, $T/2$, required for the wave to travel from the source to the thermometer is found from Equation (36) to be:

$$\frac{T}{2} = \frac{x_L^2}{2\pi\alpha} \tag{38}$$

Putting x_L equal to 1 cm, the time lags for a few substances having different diffusivities, α, are given in Table 2:

Table 2.

Substance		t(sec)
Brick	.005	32
Brick	.01	16
Brick	.1	1.6
Iron	.16	1
Aluminum	.8	.2
Copper	1.1	.15
Silver	1.7	.09

According to Equation (38), the lag depends only on the thickness of the plate and the diffusivity of the material, and not on the amplitude of the wave. Thus, again, the period of oscillation of the controller is independent of the sensitivity, assuming the dead zone is negligible.

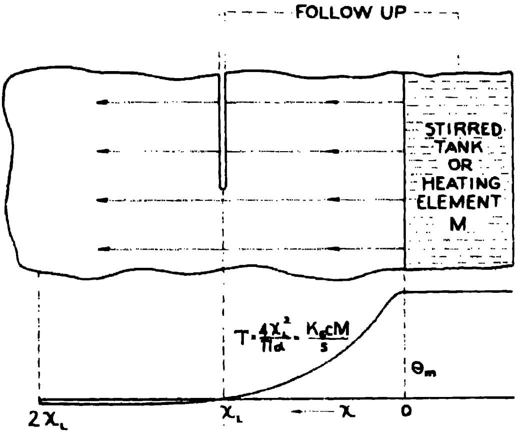
FOLLOW UP
STIRRED TANK OR HEATING ELEMENT M
$T = \frac{4x_L^2}{\pi\alpha} \cdot \frac{K_c cM}{s}$
θ_m
$2x_L$
x_L
x
0

Fig. 4. Corresponding control with attenuation of temperature and real source. Equation (39) et seq.

In Fig. 4, the heating element or source has a thermal capacity cM, and may be an electrical resistor or strongly stirred bath against the surface of the solid conductor. If x and t are measured as before, then Equation (35) can represent the temperature wave in the solid, and we must next determine the phase relation between θ_0 at the surface and q, the controlled heat input.

At $x = 0$,

$$\theta_0 = \theta_m \cos 2\pi t/T \tag{39}$$

$$\frac{d\theta_0}{dt} = \frac{q}{cM} = \frac{-2\pi\theta_m}{T}\sin\frac{2\pi t}{T} \tag{40}$$

$$2\pi\theta_m \quad \left(\frac{2\pi t}{T} + \frac{\pi}{2}\right)$$

That is, when θ_0 is a maximum, q has been positive and is passing through zero. With q thus leading θ_0 by one-quarter period and leading θ_L at the thermometer by one-half period, then the thermometer finds itself at one-quarter wave length from the surface of the solid and $T=4x_L/v$, or four times the time lag between the temperature of the source and that of the thermometer.

Referring to Equations (36) and (37), in the present case:

$$\theta'_m = \theta_m e^{\frac{-\lambda}{4}\sqrt{\frac{\pi}{\alpha T}}} = \theta_m e^{\frac{-\pi}{2}} = \frac{\theta_m}{4.8} \tag{41}$$

that is, the wave is attenuated to 1/4.8 of its initial value, whatever the value of the sensitivity of the controller, capacity of the source, or properties of the solid. But this does not determine the minimum sensitivity required to maintain oscillations.

Noting that this case resembles the so-called batch process and referring to Equations (13) *et seq.*, we may write, for small oscillations:

$$s\theta_L = -k_6 q \tag{42}$$

and

$$s\theta'_m = k_6 q_m \tag{43}$$

From Equation (40):

$$q = \frac{2\pi cM\theta_m}{T}\cos\left(\frac{2\pi t}{T} + \frac{\pi}{2}\right) \tag{44}$$

and

$$q_m = \frac{2\pi cM\theta_m}{T} \tag{45}$$

Substituting for q_m from Equation (43):

$$\frac{s\theta'_m}{k_6} = \frac{2\pi cM\theta_m}{T} \tag{46}$$

and from (41):

$$\frac{s\theta'_m}{k_6} = \frac{9.6\pi cM\theta'_m}{T} \tag{47}$$

or

$$s = \frac{k_7 cM}{T} \tag{48}$$

and from (36):

$$s = \frac{k_8 \alpha cM}{x_L^2} \tag{49}$$

In conducting the analysis of the last case toward Equations (48) and (49), it has been our purpose to show why, in the so-called batch process the sensitivity can take very high values, even in a controller having no damping arrangement. The analysis applies also to those continuous processes in which the load, or "through-put" of processed material is small compared thermally with the heat loss. Examples of such continuous processes are (1) manufacture of rubber filaments, (2) continuous heat treatment of steel wire, and (3) tunnel kiln processes for the slow firing of ceramic materials.

The last few equations, including (41), show that the attenuation of a temperature wave through the protection tube of a thermocouple in a furnace or liquid bath may be as much as 80 per cent. Thus the oscillations of the temperature of the outer surface of the tube may be some five times as great as the indicated oscillations.

We have, so far, treated a limited number of typical cases of automatic temperature control, but believe that we have demonstrated a new treatment which not only is relatively easily understood, but affords useful results reasonably approximating real cases. We believe also that the corresponding method of control stands out as the most important and most widely used, (possibly second only to "on-and-off" control), and that a study of the one method suffices for learning the fundamentals. In passing, a little consideration shows that in on-and-off control the thermometer will generally find itself one-quarter wave-length from the source, and not one-half wave, as Ivanoff [1] considered by assuming a square wave, *i.e.*, no capacity effect that is not accompanied by attenuation. Our treatment is not generally in disagreement with the descriptive method of Bristol and Peters,[7] nor with those authors who would stress the special hydraulic problems accompanying the use of a valve to control flow against varying back-pressures or resistances. It is admitted without argument that there may be a deal of engineering required for solving many of the problems in industrial process control. We are concerned here with the physics of the problems, not the mechanical design of plant, instruments or accessories. Possibly more has been written about the mechanical design of governors, or speed regulators, than about the physics of automatic temperature control, and the former should not be confused with the latter.

Nearly all problems in temperature control that are solved, have been solved experimentally, both in regard to the construction or selection of control equipment on an experimental basis, and the adjustment of the trial instruments as to sensitivity, damping, speed of automatic reset,[8] response to change of load or control point, and variations of these factors under different conditions. An analytical method of study of the theories of automatic temperature control will make for more intelligent judgment in adjusting a controller, but we would hesitate to try to solve a problem in advance of the practical trial to the point that prescribed values of the many variables involved could be set down with nicety. A practical difficulty is met, for example, in the generally unavoidable dead-zone of a controller. We have not avoided mathematical treatment of the dead zone because of indolence but because of indifference. As to that imperfection, it should be in general as small as possible.

An ideal controller for experimental study of the theory is one incorporating the Gouy principle [9] because it furnishes "corresponding" control, has no dead zone whatever, and makes possible the selection of sensitivities of exceedingly high values. It has been found to be the most satisfactory device for precision control in the laboratory by Sligh,[10] other members of the staff of the National Bureau of Standards, Roebuck,[11] and many metallurgists who are in charge of creep tests. Our treatment of corresponding control is well adapted to a study of the Gouy principle or a controller utilizing it. The sensitivity, as we have used the term, and with a meaning which is acceptable to many others, is inversely proportional to the stroke of the Gouy oscillator, which determines the limits of the throttling zone, and the sensitivity is made constant by imparting to the oscillator a motion in accordance with Equation (6). The sensitivity can be expressed also as inversely proportional to the velocity of the oscillator at any part of its stroke, and the period of oscillation is made short enough not to enter into the analysis.

Discussion

E. S. Smith, Member A.S.M.E., C. J. Tagliabue Mfg. Co., Brooklyn, N. Y.: First, to dispose of a difference of viewpoints, the present discussor as an engineer is glad to have the attention of physicists directed by one of them to the recent papers on regulation in general, which have appeared in A.S.M.E. publications, and is impelled to point out that regulation generally is more a matter of the applied mechanics of oscillating systems than of physics, temperature regulation being a possible exception, since it involves attenuation and other physical phenomena of heat transfer. In any case, the practical handling of regulation in general is ordinarily a matter of the art of mechanical engineering which may be taken as the application of the science of at least one branch of physics.

It appears to this discussor that there are two separate parts to the paper as it stands: static and kinetic treatments, and that the author should extend the treatment of sensitivity s to bridge the present gap so that the hunting relations involved for a combined regulator-and-plant of sensitivity s would be related to the s for the static treatment instead of some other, a point upon which a possible question now seems to exist.

In his treatment of the steady state, the author has a novel method of analysis which led him usefully to a novel inverse-exponential or log-log regulator which has a constant overall sensitivity over a wide operating range with both continuous and batch processes. To appreciate his contribution to this art, it must be borne in mind that then only the linear and semi-log relations were in general use. The sensitivities of these vary objectionably with a single controller under a wide range of operating conditions, although the semi-log relation approaches the author's log-log relation as a limit at infinitely high sensitivities. In many practical cases, it is important to keep the sensitivity constant at nearly the maximum value at which the regulation will be stable over a wide range of conditions, since this sensitivity is what determines the "accuracy of regulation" or maximum departure from the control point.

It is regretted that shortage of time after the receipt of the finished draft of the paper prevents any present comment on the kinetic case other than that the author's treatment of it appears to be unquestionably useful for temperature regulation and generally consistent with, and an advance over, earlier treatments. The earlier treatments were either for incomplete hydraulic analogies or for heat flow analyses which were at least incomplete as ignoring the heat capacity of, *e.g.*, the source.

The advance made by the author's work in the static case may be estimated from a comparison with the following treatment which was made by the discussor following his acquaintance with the then-unpublished manuscript of the author's static analysis. The following treatment is applicable to a linearly-throttling regulator for a continuous process.

When heating an independently variable stream of fluid, its temperature rise may be regulated by controlling the heat input rate, q.

Assuming no losses, the static or equilibrium relation for the process is, from the author's work,

$$q = L\theta \tag{1}$$

and its familiar (in thermodynamics as the gas temperature-pressure solid) rectangular-hyperbola type of "solid" is shown in the accompanying Fig. 5, in which the maximum values along the q, θ and L axes are respectively 1, 1, and 5, and in which θ_0 is an *upper* reference temperature. As in the paper, L is the thermal load in pounds per second times average specific heat.

The equation for a conventional linearly-throttling regulator is

$$\theta = \theta_0 + q(d\theta/dq) = \theta_0 + q/m, \text{ putting } m = dq/d\theta \tag{2}$$

or

$$q = m(\theta - \theta_0) \tag{2a}$$

This relation is seen in Fig. 5 as an inclined plane having a slope of -0.06 with the qL plane, or a value of $m = -1.67 \frac{\text{B.t.u.}}{°\text{F sec.}}$

The corresponding equation for the regulated process is, equating (1) and (2a)

$$L\theta = m(\theta_i - \theta_o) \tag{3}$$

the actual temperature θ being that indicated, θ_i.

To find the overall sensitivity, s, differentiate (3) taking L as a constant.

$$L d\theta = m d\theta_i \tag{4}$$

and

$$s = \frac{-d\theta}{d\theta_i} = \frac{-m}{L} \text{ [cf. author's equation (1)]} \tag{5}$$

where, as in the author's treatment, the controller change, $d\theta_i$, is the cause, the resultant temperature change, $-d\theta$, of the system is the effect, and the sensitivity, s, is the ratio of the effect $-d\theta$ to its cause $d\theta_i$ in the same units, the minus sign being necessary with a controlling action. The regulated system's overall sensitivity is thus seen to vary inversely with the load with a conventional throttling regulator.

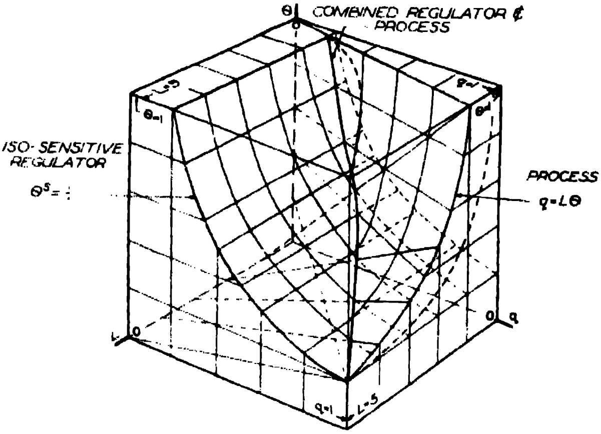

FIG. 5.

Corresponding control of the continuous process (Equation 2a of discussion).

Fig. 6 was likewise prepared by the discussor to show how the same process would be regulated by the author's improved regulator which gives constant overall sensitivity for the combined regulator-and-process. A comparison of the two figures shows that the performance of the author's iso-sensitive regulator departs widely from the conventional linearly-throttling design. The paper appears to need a figure which shows the relations for the batch process, an omission which the author is requested to remedy in his reply.

Reply

Although the author stated in the paper that "we do not propose to use the above (static) equations for a study of dynamic conditions, because their combination with harmonic functions would lead to cumbersome forms," he readily admits that further explanation of the use of s for sensitivity in the "kinetic treatments," is in order, although but one meaning is employed throughout.

In the paper, following Equation (21), the statement is made that *"for small variations,"* $s\theta_L=-\theta_0$. Thus, if the controller is designed according to Equation (6), the treatment following Equation (21) is valid only for small variations.

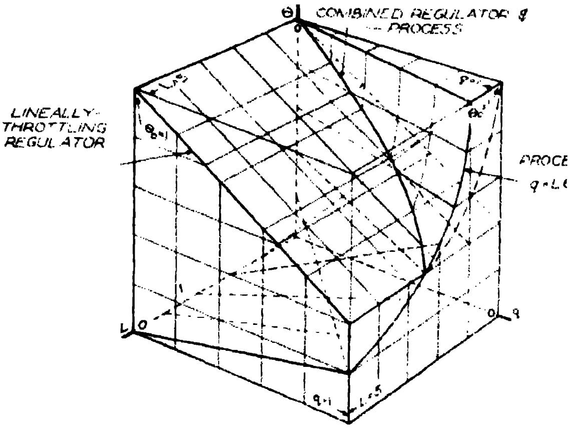

FIG. 6.

Corresponding control of the continuous process. Putting $\theta_0=0$ in Equations 2, 6, and 7 of the paper.

This does not mean, however, that the treatment lacks practical significance. On the other hand, it is applicable with sufficient approximation to temperature oscillations of appreciable magnitude, for example, having an amplitude of 20° with an available range of 1000°, unless s is large. If s is large and the oscillations result in very large variations of heat input, the temperature waves will depart noticeably from the simple harmonic form. This is a condition that is generally avoided. The ordinary condition of small oscillations, which accompany a selection of a value of s slightly larger than necessary, will be exhibited with constant amplitude at various loads.

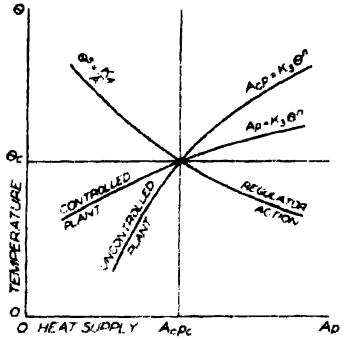

FIG. 7.

Corresponding control of the batch process. Equations 9, 14, and 18.

In one case we are interested in small departures of temperature from a selected value, and in another constancy of sensitivity throughout the full range of action of control.

It is readily apparent that the relation $s\theta_L=-\theta_0$ defines s according to Equation (5) of the discussion. Hence the kinetic treatment applies for oscillations of a "linearly-throttling" regulator, the load having been taken as a constant, L_1. While the oscillations of this regulator do not change their form with amplitude, the amplitude will change with load because s is not a constant.

The discussion would have been slightly clearer if m had been taken as positive, and Equation (2a) had been written:

$$q - q_0 = -m(\theta - \theta_0)$$

where q_0 is the heat required to maintain a temperature θ_0, the control point. This equation reveals the action of an automatic controller that lowers the input of heat if the temperature is above the control point, and conversely. This action is completely hidden in Equation (2a), which Mr. Smith calls "the equation."

The writer appreciates very much Mr. Smith's careful discussion and pertinent suggestions. In answer to his request we include Fig. 7, showing the action of a corresponding controller about the control point θ_0, of a batch process, requiring a normal heat input $A_0 p_\sigma$.

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Automatic Control of Laboratory Furnaces by the Wheatstone Bridge Method

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Furnace temperature regulators that use a thermocouple or radiation pyrometer for the temperature-sensitive element are widely used and their behavior is well understood. However, in many electric furnaces the resistance of the heating element changes rapidly with temperature and maintains a definite relation to the temperature. Hence, with these furnaces it is possible to use the winding of the furnace itself as the temperature-sensitive element, thus avoiding the need for locating any part of the regulator inside the furnace or for making any connection to the system used for measuring the temperature.

The earliest application of this principle to the control of high temperatures appears to have been made by White and Adams [1] at the Geophysical Laboratory about 1911. They connected the furnace winding as one arm of a Wheatstone bridge whose galvanometer worked a relay in the power circuit.

This first attempt gave surprisingly close regulation, and subsequent developments [2] have been aimed, chiefly, at making the apparatus more reliable for long runs.

The principal application of these regulators has been to small laboratory furnaces with a heating element of platinum or platinum-rhodium wire. The wire is wound in a single helix on the outside of an alundum tube and is completely covered with a layer of alundum cement. The finished tube is surrounded by several centimeters of calcined magnesia. To obtain a flat maximum in temperature distribution along the axis of the tube, the length of the winding is made five or more times its diameter.

Resistance measurements on several furnaces of this type can be expressed fairly well, above 500 °C, by the relation:

$$R \propto (t_0 + t)$$

where t_0 is a constant, for any one furnace, having a value between 400 and 700°. Thus the resistance approximately doubles in going from 500 to 1500°. The resistance change for platinum-rhodium windings is somewhat smaller. The method is not very satisfactory with alloys such as Chromel and Nichrome because of their low temperature coefficients.

Below about 1000° the resistance-temperature relation of platinum changes very slowly with time. At higher temperatures, changes in the furnace cause a slow drift, and the temperature maintained by the regulator usually falls gradually. The drift is less rapid with platinum-rhodium than with platinum, particularly at the higher temperatures.

Direct-current Operation

An early modification of the original White and Adams circuit is shown in Fig. 1. The temperature setting is made by adjusting the value of C so that the bridge is balanced when the furnace is at the desired temperature. Then the line rheostat is set so that the furnace receives too much current when the main relay is closed and too little current when it is open. When the regulator is running, the temperature of the winding oscillates over a short interval with a period of a few seconds, but in the interior of the furnace the amplitude of this oscillation is usually very small.

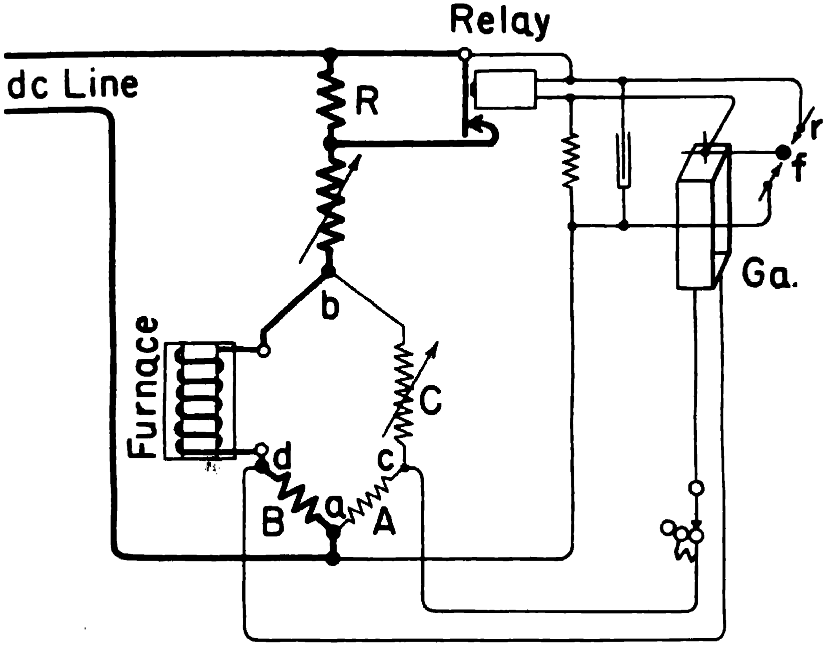

FIG. 1. Simple temperature regulator used with direct current.

Most of the irregularities in the behavior of these early regulators seemed to come from deterioration of the galvanometer contacts. With the advent of radio broadcasting, electron tubes became common, and we adopted one of them to serve as an intermediate relay[3] between the galvanometer and the power relay. The operating current of the tube is exceedingly small and contact troubles are much less frequent. There seems to be an advantage, however, in making resistance R_1 (Fig. 2) small enough to provide an initial surge of several milliamperes when the contacts close.

Alternating-current Operation

The regulator may be adapted for use on an alternating current line in either of two ways:

(1) We may employ an a.c. galvanometer, or we may use the original d.c. galvanometer with a suitable rectifier. In these regulators, as in the d.c. form, the mean power input is adjusted by a magnetic relay, which alternates a high power level with a low level.

(2) We may adjust the power input with a saturating reactance and thyratron, using an amplifier to build up the output of the bridge to the much larger voltage needed at the grid of the thyratron. In this form of regulator there are no moving

contacts and it is therefore more reliable. In addition, a high sensitivity is easier to obtain with the amplifier than with the galvanometer.

When the bridge is supplied with direct current the galvanometer voltage E_{cd} (Fig. 1) becomes zero when the furnace is at such a temperature that its resistance satisfies the proportion:

$$F/B = C/A$$

At a slightly higher temperature, $t + \Delta t$, its resistance has the value $F + \Delta F$ and

$$E_{cd} = -\frac{B\Delta F}{B + F} I_F \tag{1}$$

where I_F is the current in the furnace winding.

With alternating current the galvanometer voltage does not become zero unless the four reactances, X_A, X_B, X_C, X_F, as well as the four resistances, are balanced. If the reactance in each arm is small in comparison with the resistance in that arm, and $\Delta F/F$ is small, the galvanometer voltage vector

$$E_{cd} = -\frac{B\Delta F}{B + F} I_F - \frac{(BX_F - FX_B)I_F - (BX_C - FX_A)I_C}{B + F} \tag{2}$$

where I_F and I_C are the currents in the two sides of the bridge.

The first term is a vector in phase with the bridge voltage E_{ab}; its magnitude is the same with alternating as with direct current and it passes through zero when the four resistances are in proportion. The second term is a vector 90° from E_{ab}, and for this approximation may be assumed to remain constant in amplitude while the in-phase component varies through zero.

Galvanometer Type of a.c. Regulator

Most of the regulators in use at present differ only in details from the form[4] described in 1925. They employ the original d.c. galvanometer with a simple synchronous rectifier whose function is to rectify the in-phase component of the galvanometer voltage, leaving the 90° component unrectified. The galvanometer then behaves exactly as it did in the d.c. regulator except that with this half-wave rectifier the deflection is only half as great.

A typical circuit is shown in Fig. 2; it includes the electron tube intermediate relay mentioned above.

The bridge circuit is like the one commonly used in commercial test sets, but unlike these sets the bridge needs to dissipate considerable power. The values of resistance used in the three arms depend on several factors; voltage and current required by the furnace when at its maximum temperature, available line voltage, and the galvanometer coil resistance. The values listed below Fig. 2 were calculated for a furnace requiring a maximum of 10 amperes at 80 volts from a 115-volt line. In this regulator, coil B has two 1-ohm sections of 0.25″ by 0.016″ advance ribbon wound on a 12″ length of 2¼″ alundum tubing. In each section the ribbon is doubled back on itself to form a second, reversed layer, insulated from the first with thin mica. It will safely carry about 15 amperes.

The resistance values chosen for arms A and C are the result of a compromise between galvanometer sensitivity and the current-carrying capacity of available commercial coils and decades. The thirteen 100-ohm coils of A and C are mounted in the open to facilitate cooling, and the lowest dial of C is a 10-ohm circular rheostat having 100 scale divisions.

The rectifier will not in general be exactly in phase with the bridge voltage but will differ by a small angle ϕ'. Its output voltage does not become zero until the bridge becomes sufficiently unbalanced to make the true in-phase voltage equal to the product of the 90° component into the tangent of ϕ'. This does no harm so long as ϕ' and the 90° component are constant and not too large; but it may cause serious trouble with a poorly constructed mechanical rectifier.

A vacuum-tube dynamometer is being used in several regulators in place of the vibrating reed rectifier described here. The dynamometer employs four triodes coupled to the bridge through a step-up transformer. The dynamometer behaves as a full-wave rectifier. Although this modification is more than twice as sensitive as the one described, the slow change in vacuum tube characteristics causes a slow temperature drift which may be objectionable.

At least one regulator makes use of an a.c. galvanometer which employs a beam of light and a phototube in place of moving contacts.

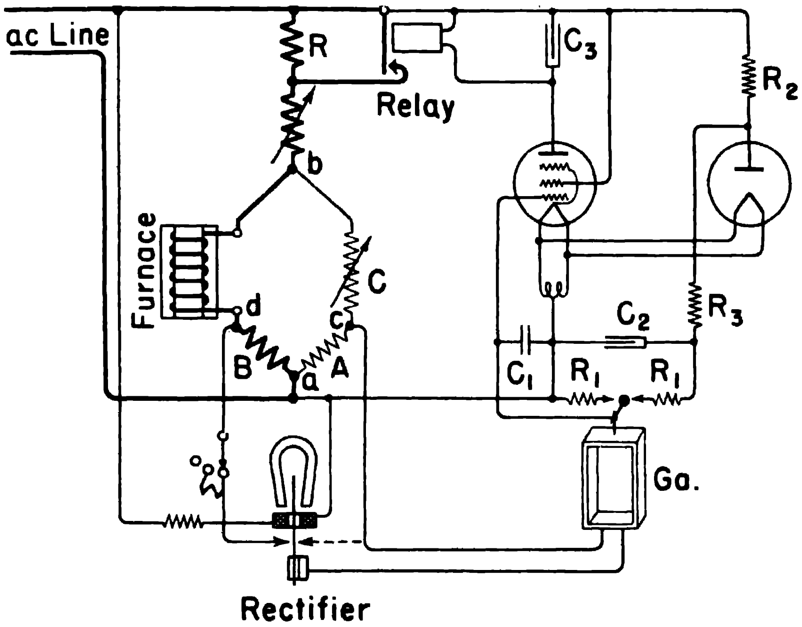

FIG. 2. Galvanometer-type regulator; 115-volt, a.c. line. Furnace resistance (in operation), 2 to 13 ohms, maximum current, 15 amperes. *A*, 100 ohms; *B*, 1 ohm; *C*, 200 to 1310 ohms in steps of 0.1 ohm. *R*, a bank of 32-volt, 100-watt tungsten-filament lamps. R_1, 10,000 ohms; R_2, R_3, 0.1 megohm. C_1, 0.1 mfd; C_2, 1 mfd; C_3, 2 mfd. Galvanometer coil, 50 ohms; relay coil, 2500 ohms, about 10 ma. A Type-47 pentode is satisfactory for the relay tube and another "47" may be used for the diode rectifier, connecting screen and control grids to the plate.

Thyratron Form of a.c. Regulator

A circuit diagram for the thyratron form of regulator is shown in Fig. 3. The bridge is the same as in Fig. 2; however, since the amplifier is a voltage-operated device, we may now make the resistance in *A* and *C* very much greater. A tenfold increase avoids all danger of overheating without using resistances so high that the coils may be unstable.

If the voltage that controls it is not too small, the response of the thyratron is determined by the phase angle of this voltage rather than by its amplitude. The thyratron then behaves very much like a continuously variable rheostat whose setting is given by the phase angle. The controller is thus of the throttling type and our problem is to obtain the required changes in phase angle with satisfactorily small changes in furnace temperature.

The phase angle, ϕ, between the galvanometer voltage, E_{cd}, and the bridge voltage, E_{ab}, is the angle whose tangent is the ratio of the two components of E_{cd}. We obtain from Equation (2):

$$\tan \phi = \frac{(BX_F - FX_B)I_F - (BX_C - FX_A)I_C}{B\Delta FI_F} \tag{3}$$

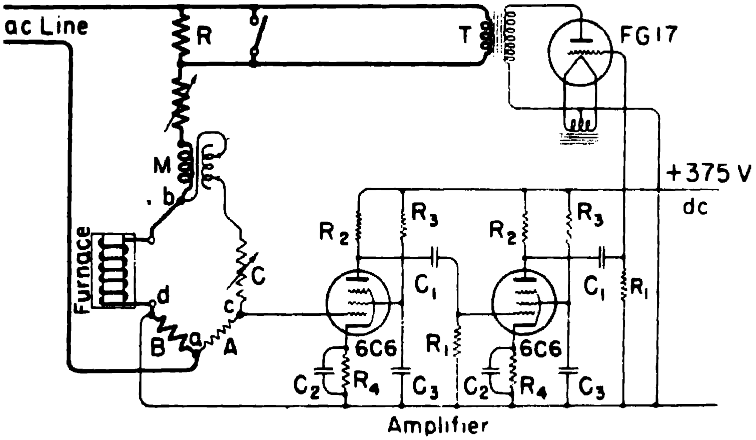

FIG. 3. Thyratron-type regulator; 115-volt, 60-cycle line. Furnace resistance (in operation), 2 to 13 ohms; maximum current, 10 amperes. A, 1000 ohms; B, 1 ohm; C, 2000 to 13,100 ohms in steps of 0.3 ohm. R, a variable rheostat set to give an RI drop of about 25 volts when the thyratron is not conducting. (The lamp-bank used in the galvanometer-type regulator is not satisfactory here.) A useful form of rheostat has several coils with individual switches arranged to connect any desired number of coils in parallel. T, a 60-cycle, 250-volt-ampere transformer, primary 25 volts, secondary 1000 volts. R_1, R_3, 1 megohm; R_2, 0.2 megohm; R_4, 1500 ohms. C_1, 0.01 to 0.05 mfd; C_2, 25 mfd; C_3, 0.25 mfd. The optimum capacity for condenser C_1 must be determined by trial. If it is too large, the thyratron may continue to conduct when the temperature setting is suddenly reduced; if too small, the throttling zone is narrowed.

where I_F and I_C are the currents in the two arms of the bridge. For values of ϕ near 90° (the bridge nearly balanced) the change in ϕ is nearly proportional to the change in furnace temperature and inversely proportional to the magnitude of the 90° component.

Having bifilar wound bridge coils we may neglect X_A, X_B, and X_C, and Equation (3) becomes:

$$\tan \phi = X_F/\Delta F = X_F I_F/\Delta F I_F$$

Although the absolute magnitude of X_F in the typical furnace is low, it is large enough to make the simple bridge of Fig. 2 too insensitive for satisfactory phase shift control. This may be remedied by adding an adjustable inductance to arm B or arm C or, as seems better, a mutual inductance connected as in Fig. 3. The primary of the mutual inductance carries the whole bridge current, $I_F + I_C$, and is outside the bridge, while the secondary carries only the current I_C. The total

90° voltage across the secondary is $\omega M(I_F + I_C) + \omega L_S I_C$. I_C, however, is here small in comparison with I_F; L_S, the secondary inductance, is of the same order as M; therefore we may neglect terms in I_C, obtaining the value $\omega M I_F$ for the 90° voltage. Since this voltage is applied in arm C of the bridge we may substitute it for the voltage $X_C I_C$ in Equation (3). Then, substituting for X_F its value ωL_F, we obtain:

$$\tan \phi = -\frac{\omega(L_F - M)}{\Delta F} \tag{4}$$

Substituting in Equation (2) for the galvanometer voltage, we obtain:

$$E_{cd} = -\frac{B\Delta F}{B + F} I_F - j\frac{B\omega(L_F - M)}{B + F} I_F \tag{5}$$

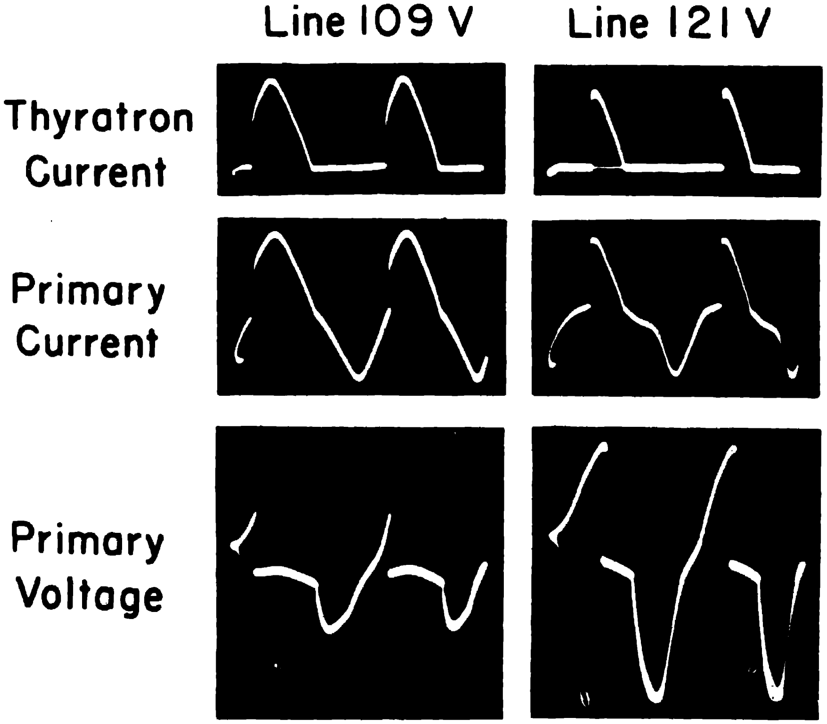

FIG. 4. Oscillograms illustrating behavior of the saturating reactance when the regulator is in operation. The temperature of a furnace was being maintained a little above 820 °C.

The sensitivity of the regulator increases as the value of $(L_F - M)$ is diminished, but at the same time the minimum value of E_{cd} (when $\Delta F = 0$) decreases. At some value of M the amplified voltage becomes too small for phase shift control of the thyratron and there is no further gain in sensitivity.

The primary winding of M is a single layer of heavy wire having an inductance a little greater than the inductance calculated from the furnace dimensions. The tapped secondary occupies the v-shaped helical groove between the primary turns and there is a narrow strip of transformer sheet that can be turned inside the coil for close adjustment of the induced voltage.

The amplifier is of the conventional resistance-capacity coupled type. It has a gain of about 20,000. A total phase shift of +20° to +30°, at the line frequency, is desirable.

The 40 to 1 step-up transformer *T* associated with the thyratron functions partly as a transformer and partly as a saturable reactor. If the phase of the control voltage is such that no plate current flows in the thyratron, *T* is simply an unloaded transformer. A negligibly small magnetizing current flows in its primary, and the primary voltage is practically the product of the whole bridge current into the resistance *R*; *i.e.*, about 25 volts for a 115-volt line.

If the thyratron is caused to conduct during a part of each cycle, the secondary voltage during this interval is limited to the 15 to 20 volt tube drop, and the primary voltage to about 1/40 of this. Most of the bridge current is being diverted from resistor *R* to the transformer. Since current flows through the thyratron in one direction only, the transformer becomes partly saturated and a considerable fraction of the bridge current is diverted from *R* during the rest of each cycle, while the thyratron is not conducting. Thus the voltage drop across *R* is adjusted to maintain the required voltage at the furnace terminals.

The oscillograms in Fig. 4 were made at two different line voltages with the regulator operating. The upper curves show the unidirectional current pulses in the thyratron. The middle pair, to a reduced scale, combine the pulses due to thyratron current with a magnetizing current flowing in the opposite direction during the intervals when the thyratron current is zero. These oscillograms were made while the furnace was being held a little above 820 °C. Equilibrium temperatures for the two line voltages were found to differ by 0.14°.

The effect of ambient temperature on furnace temperature is usually small. It has been compensated over a wide range of furnace temperature by the change in resistance of a copper coil placed in arm *C* of the bridge. The copper wire was wound on a metal spool and the coil mounted in the open, near the bridge coils. It was then found necessary to increase its thermal lag by a covering of friction tape to make it respond to temperature changes at about the same rate as the furnace.

Summary

The Wheatstone bridge type of temperature regulator is particularly suitable for controlling the long, narrow, platinum-wound furnaces used where the temperature of a small charge must be known accurately. The two types of regulator in general use at the Geophysical Laboratory are discussed in detail.

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An Electronic-Contacting Galvanometer for Temperature Control

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This paper describes a modification of a galvanometer enabling it to control sufficient energy to operate a small power relay, shows the precision obtained with one controlling system using this galvanometer, and describes a simple modification to improve the sensitivity.

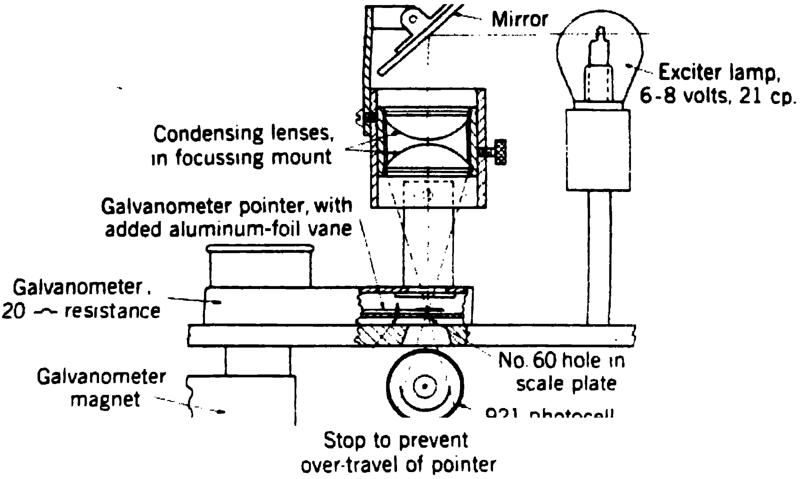
A portable potentiometer was converted by Walsh and Milas [1] into a temperature controller by adding a phototube and associated equipment. In the apparatus to be described here it was not desirable to limit the usefulness of the equipment to one potentiometer; therefore a contacting galvanometer was constructed as a unit such that it could be used with any existing apparatus requiring a galvanometer.

Construction of Contacting Galvanometer

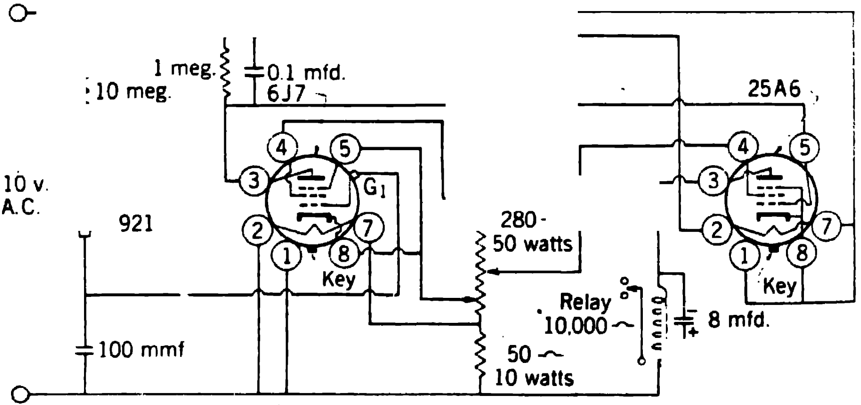
The "hole-in-meter" principle is utilized in this instrument. A beam of light is projected through a small hole drilled in the scale of a rugged galvanometer, such that movement of the galvanometer pointer near balance interrupts the light flux passing to a phototube below the scale. This change in light flux is converted by the phototube into a voltage variation that is amplified sufficiently to operate a relay. Thus, a small movement of the galvanometer pointer is converted into movement of a relay armature without in any way impeding the normal action of the galvanometer pointer. The exciter lamp, optical system, galvanometer, phototube, amplifier, and primary relay making up the contacting galvanometer are built into a compact unit which is operated from 115 volts a.c. and is at least as rugged as a conventional portable potentiometer. The cost of the components, including a relay capable of handling 1.5 amperes at 115 volts a.c., is approximately $40.00.

Fig. 1a shows the construction of the optical unit of the instrument. The 1¼-inch focal length of the condenser system of two lenses 1 inch in diameter fixes the relative spacing of parts; the mirror reduces the overall height of the instrument. A vane of aluminum foil ¼ inch wide is cemented to the galvanometer pointer; a stop is provided to prevent reversed operation as the result of a severe overshoot. The optical system is adjusted by focusing the smallest possible point of light on the aluminum vane in a position such that, with the pointer withdrawn, the diverging beam enters the hole in the scale. Maximum sensitivity corresponds to the minimum possible dimension of the beam at the level of the vane, a small galvanometer deflection producing a large change in light flux.

Fig. 1b is the schematic diagram of the amplifier. The circuit was suggested by Shepard,[2] and has the advantages of simplicity and sensitivity; it can detect relatively small amounts of light, which makes it especially suitable to this application. The 921 cartridge-type gaseous phototube has a compact structure, greater sensitivity than the vacuum-type phototube, and high sensitivity in the red end of the spectrum. Thus, the 21-cp. 6-8-volt automobile-type exciter lamp could be operated at 4.0 volts and yet furnish ample light for satisfactory operation. Because the voltage applied to the phototube may be greater than its glow discharge potential, a 10-megohm current-limiting resistor was added to its anode circuit.


Mirror
Exciter lamp, 6-8 volts, 21 cp.
Condensing lenses, in focussing mount
Galvanometer pointer, with added aluminum-foil vane
Galvanometer, 20 Ω resistance
Galvanometer magnet
No. 60 hole in scale plate
921 photocell
Stop to prevent over-travel of pointer

A. Galvanometer and optical unit



B. Schematic diagram of amplifier unit

FIG. 1. Design of contacting galvanometer.

Sensitivity of Contacting Galvanometer

The sensitivity of the contacting galvanometer was measured in a potentiometer circuit by varying the input voltage over the range required to operate the relay. The voltage was changed by adjusting the current in a 1-ohm resistance across the potentiometer input terminals. At each movement of the relay armature the input voltage was measured with a potentiometer having a sensitivity of 1 microvolt, the average of twenty such determinations giving a difference in voltage of 5 microvolts, which for the 33-ohm galvanometer is equivalent to a galvanometer current difference of 0.15 microampere. The corresponding temperature differences for various thermocouples of 1-ohm resistance are, for copper-constantan 0.16 °F, for Chromel-Alumel 0.22 °F, and for platinum-rhodium 0.77 °F. Thus, with a platinum-rhodium thermocouple, the relay would operate at ±0.4 °F from the desired temperature.

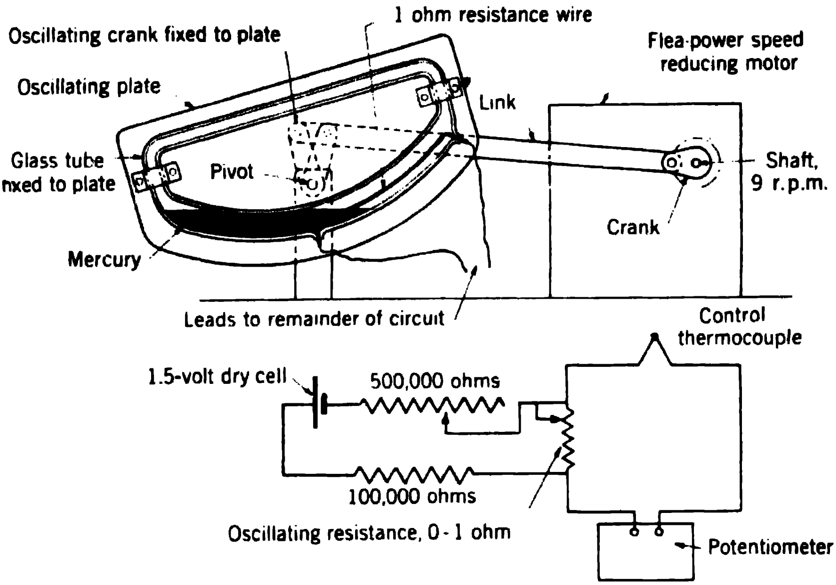

1 ohm resistance wire
Oscillating crank fixed to plate
Flea-power speed reducing motor
Oscillating plate
Link
Glass tube fixed to plate
Pivot
Shaft, 9 r.p.m.
Crank
Mercury
Leads to remainder of circuit
Control thermocouple
1.5-volt dry cell
500,000 ohms
100,000 ohms
Oscillating resistance, 0-1 ohm
Potentiometer

FIG. 2. Construction of Gouy modulator and circuit for producing voltage oscillations.

This difference, or dead zone, can be decreased—that is, the sensitivity can be increased—by (1) increasing the length of the pointer of the galvanometer, (2) using a more sensitive galvanometer, (3) using a more precise optical system, (4) increasing the light output of the exciter lamp, or (5) using a more sensitive amplifier. Each of these changes would entail either considerably greater initial cost or increased attention during operation. The contacting galvanometer used is not critically sensitive to vibration; increase in its sensitivity would require special supports or other damping means to reduce the effects of vibration. If greater sensitivity is required, it usually will be found to be more satisfactory to retain compactness and portability in the contacting galvanometer and to add a Gouy modulator.

Gouy Modulator

The temperature differences previously listed represent the limits at which the contacting galvanometer will operate. They also represent the best possible temperature control obtainable with this instrument. Objects of high heat capacity in a furnace do not exhibit the same temperature fluctuations as the furnace unless the period of temperature fluctuation is long. Therefore, a method for decreasing the period of such fluctuations is desirable; this is equivalent to increasing the sensitivity of the instrument.

The method utilized was based on a principle originally described by Gouy[3] and later by Sligh[4] by which the heat input to a constant-temperature apparatus is increased for intervals proportional to the temperature difference between the apparatus and that to which the control is set. The thermoregulator used by Gouy and by Sligh consisted of a bulb filled with an expansible liquid and connected to a glass U-tube partly filled with mercury, the rise of the mercury completing an electrical circuit through a contact to control the energy input to the apparatus. Gouy's modification was to substitute a mechanically driven oscillating contact for the upper fixed one ordinarily used; he reported a gain of 20 to 1 in sensitivity for an ordinary laboratory water bath.

This principle was applied to the contacting galvanometer by adding an oscillating voltage to the thermocouple voltage instead of mechanically driving the galvanometer, so that at balance the pointer moved periodically about its true mean position. This oscillating voltage was produced by passing a small current through a resistance periodically varied from zero to 1 ohm by the movement of mercury over a resistance wire. The construction of the apparatus is shown in Fig. 2; a glass tube containing mercury and a resistance wire is oscillated at 9 cycles per minute by a "flea-power" motor and a simple linkage. The circuit shown in the figure provides for a voltage drop in the resistance of 2.5 to 15 microvolts, dependent on the setting of the 500,000-ohm variable resister.

Sensitivity of Modified Contacting Galvanometer

A typical use of the completed instrument was the control of the temperature of a silicon-carbide tube furnace 2 by 3 inches in diameter and 12 inches in length, operating at 2,000 to 2,900 °F. A platinum-rhodium thermocouple placed to receive direct radiation from the inner furnace wall was connected through a potentiometer to the contacting galvanometer. The effectiveness of the unit as a temperature controller was tested by means of a second thermocouple connected to the precision potentiometer. Both thermocouples were of 0.6-mm wire supported in 2-hole porcelain tubing of equal lengths. The zone of uniform furnace temperature was 3 inches, at the center of which the couples were set; thus both couples were assumed to be at the same temperature. The contacting galvanometer operated a power relay that could short part of the resistance in the power circuit of the furnace; the changes in energy input were high enough so that normal fluctuations in supply voltage did not exceed the controlling ability of the contacting galvanometer.

Fig. 3a indicates typical operation without the Gouy modulator, where adjustment of the energy inputs was such as to produce similar heating and cooling rates. At *A* the furnace temperature has decreased to the lower limit of the dead zone, and the energy input is increased. The furnace continues cooling for approximately 5 seconds, until the increased heat release in the silicon-carbide heating element has eventually begun to raise the temperature on the inner surface of the furnace tube. The temperature of the thermocouple then increases until at *B* the galvanometer operates, lowering the energy input, but the temperature continues to rise until the decreased energy input is effective at the inner tube surface, and then falls, until at *C* the cycle is repeated. Thus, although the contacting galvanometer sensitivity is only 5 microvolts, the resulting change in furnace temperature is 14 microvolts. The overshoots of the furnace can be decreased by adjusting the difference in energy input more closely in which instance change in supply voltage or furnace-heat loss may cause loss of control. Placing the thermocouple in the mass of silicon carbide or—with furnaces utilizing platinum resistance windings—placing the thermocouple in contact with the winding would be effective in decreasing overshooting.

Fig. 3b shows the control obtained with the Gouy modulator, the input-energy change being the same as in *A*. The sinusoidal line illustrates the voltage at the input terminals of the potentiometer as the resultant of both the thermocouple voltage and the varying voltage drop across the oscillating resistance. Between points *D* and *E*, the furnace temperature remains essentially constant, and the input energy is varied periodically so that approximately one full cycle of operation occurs during the interval normally required by the furnace to reach its greatest deviation after a change in input energy. Thus, fluctuations of the furnace temperature between changes in energy input are small, approximately 1 microvolt. At point *E*, the temperature increased as the result of an increase in line voltage, and the next cycle of decreased energy input is prolonged beyond that of normal operation as between *D* and *E*. Cooling thus begins at *F* and may continue until *G*, when the reversed action will return the furnace temperature to the correct value. In a test in which the line voltage fluctuated considerably, the maximum change in furnace temperature observed with the Gouy modulator operating was 5 microvolts; with a reasonably constant voltage supply, the change usually did not exceed 2 microvolts. For maximum effectiveness it was found that the oscillating voltage

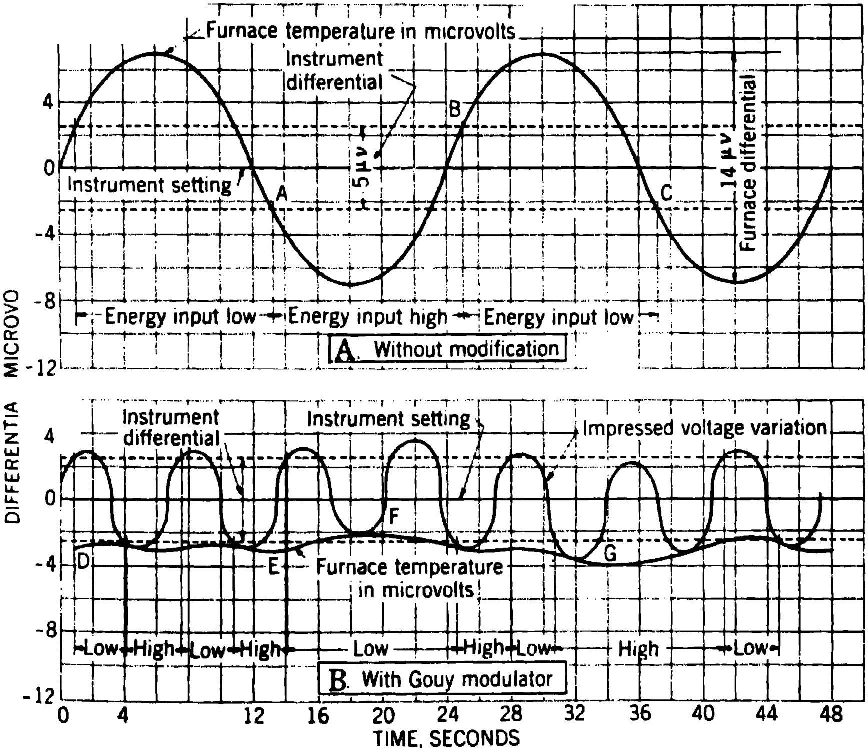


FIG. 3. Performance of temperature controller.

should be so adjusted that it is only 10 to 20 per cent greater than the dead zone of the contacting galvanometer.

To know the exact temperature of control to the same degree of accuracy as is the control ability of the instrument, refinements in temperature measurements are required. The method used and the ability to predict or to determine the temperature of the furnace, or an object in it, with a degree of accuracy comparable to the range of control, will depend on the particular application of this control instrument.

Discussion

C. O. Fairchild: The author's contribution to the symposium is valuable not only in calling attention to the possibilities of the Gouy method of control, but in the quantitative data recorded for future reference. These would be more nearly completed if the "high and low" values of heat input and the high and low temperatures, corresponding to these values applied steadily, were included.

The "hole-in-meter" principle described by the author might be called the light-interrupting principle, one that was used by Roebuck[5] in 1932, and was patented by O. E. Winter in 1926. Roebuck also included the Gouy modification with considerable success, with an additional arrangement for automatically resetting the heat input to compensate for a permanent change in heat demand. Roebuck's arrangement is somewhat more difficult to construct, but it avoids the use of a stop for the galvanometer.

The Gouy method is found in the Tirill vibrating voltage regulator, the Parsons "puff governor" and some arrangements of "astatic electronic voltage regulators" as they are described by Gulliksen and Vedder.[6] The advantages of the Gouy method are described by the present discussor,[7] stressing the fact that in it there is no measurable dead zone.

The circuit of Fig. 1b can be simplified by using a single triode and the more advantageous vacuum phototube as we are doing in a commercial instrument, requiring less power in the lamp, but a mirror galvanometer having a greater effective sensitivity, resulting in a dead zone (for on-and-off control) of 1 to 15 microvolts. Tests of the commercial Gouy modification of this same instrument have shown that a temperature constant to a few thousandths of a degree is readily attainable under favorable conditions.

In reference to the statement of the author that the galvanometer used is not "critically sensitive to vibration," we believe that any such double suspension galvanometer is thus critically sensitive in the sense that it can vibrate in resonance with various frequencies. The mirror galvanometer is not necessarily more sensitive than the pointer galvanometer, particularly because the center of percussion of the former is the closer to its center of gravity.

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A High-Temperature Thermostat

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Thermostated baths for use near room temperature have been brought to a high state of perfection and are available in almost every laboratory. The thermostated medium is usually water. By using higher-boiling liquids such as petroleum oils, vegetable oils or the diphenyl-diphenyl oxide eutectic as the thermostated liquids it is possible to obtain satisfactory results up to about 200 °C. Above 200 °C molten metals or salts may be used with varying degrees of satisfaction.

At the higher temperatures, a metal block provided with an opening into a central constant-temperature zone offers certain advantages over a liquid as a thermostated medium. Over a period of years a satisfactory thermostat of this type has been evolved in the Research Laboratories of the Universal Oil Products Company. Many minds have contributed to the present design.

The Metal Block

To be satisfactory for use as a thermostated medium the metal should have certain properties.

(1) It should have high heat conductivity.
(2) It should have high heat capacity.
(3) It must have a melting point above the range in which it is to be used.
(4) It should not oxidize or scale at the temperature of use.
(5) It should be easily machined and worked.
(6) It should be readily available.

In many instances aluminum meets these specifications quite nicely. We have used aluminum blocks up to 500 °C with complete satisfaction. Above this temperature difficulties arise due to the low melting point (660 °C) of aluminum.

Considerable study was devoted to the use of copper blocks for higher temperatures. These were found to oxidize and scale badly. When electric heating elements were used with the copper blocks, the copper oxide scale short-circuited the heating elements causing troublesome and expensive repairs. Chromium plating of the copper was a temporary but not a permanent solution.

The brasses tested gave the same difficulties. The bronzes, however, seemed to offer definite advantages. An aluminum bronze containing about 90 per cent copper and 10 per cent aluminum was found to be free from the oxidation encountered with copper; its melting point (1050 °C) is only slightly lower than that of copper (1083 °C) and the other specifications are met satisfactorily. Thermostated blocks of aluminum bronze have been used continuously at 700 °C, and for short times at 800 °C. Since this metal is also satisfactory in the temperature range where aluminum can be used, we have abandoned the use of aluminum altogether.

For still higher temperatures (up to 1000 °C) 18-8 chromium-nickel steel blocks have been used, but our experience with these blocks is quite limited.

Temperature Control

Temperature control in all cases has been accomplished by using materials having different coefficients of thermal expansion. A hole is drilled in the metal block and a porcelain rod inserted in the hole. The difference in the thermal expansion of the metal block and the porcelain rod will move one end of the porcelain rod in or out of the block slightly. This motion is transferred to a lever which is equipped with electric contacts. It has been found convenient to have the electric contacts operate a relay which controls the current to the heating element surrounding the block.

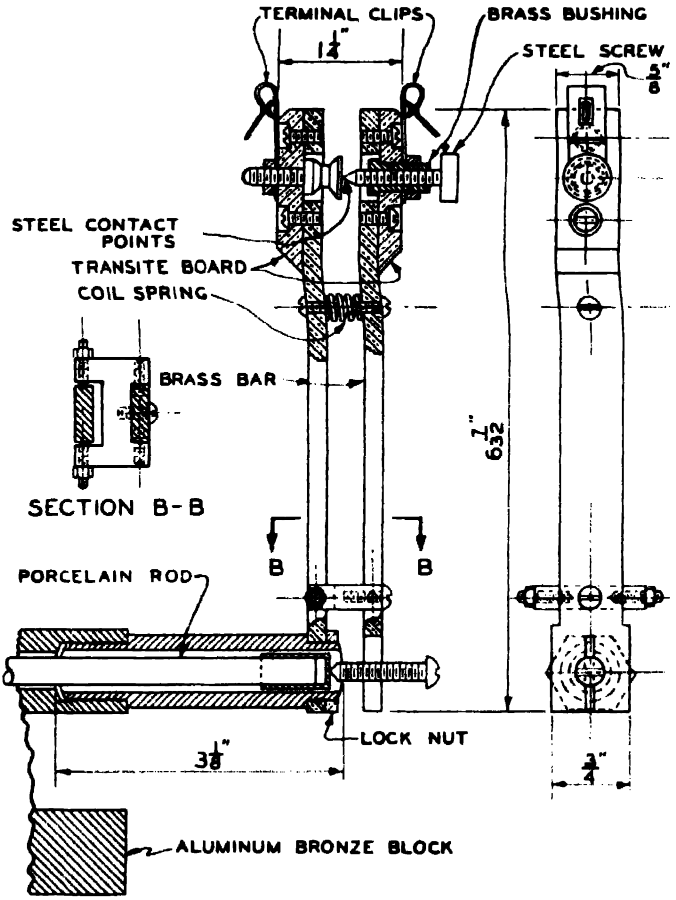

FIG. 1. Mechanism for automatic electric temperature control.

Fig. 1 gives the details of construction of a simple type of temperature controller, showing the porcelain rod in the block, the construction of the lever system, electric contacts, and the method of attaching the lever system to the metal block and the porcelain rod. An adjusting screw is provided for contact of the lever arm with the end of the porcelain rod. In bringing the furnace up to temperature this screw is tightened to keep the electric contacts closed. When the desired temperature is reached, this screw is adjusted by trial and error to just make or break the contacts by a slight movement.

For reasons of safety the use of exposed electric contacts has proved to be objectionable in some instances. In Fig. 2 the construction details are given for a controller using a totally enclosed microswitch instead of open contacts. The operation of this controller is the same as that of the one just described.

Using the construction of either Fig. 1 or 2 it is necessary to loosen the adjusting screw in contact with the porcelain rod when shutting down the thermostat. Unless this is done the contracting metal block will push the porcelain rod outward with such force that the temperature control mechanism is bent out of shape or broken, or the porcelain rod is broken. In cases where loosening this screw is inconvenient or is likely to be forgotten, the modification shown in Fig. 3 has been used. In this case the spring *A* is compressed when undue force is exerted on the porcelain rod by the cooling metal block. When the block is reheated the temperature returns almost to the original value so that only a slight adjustment is necessary.

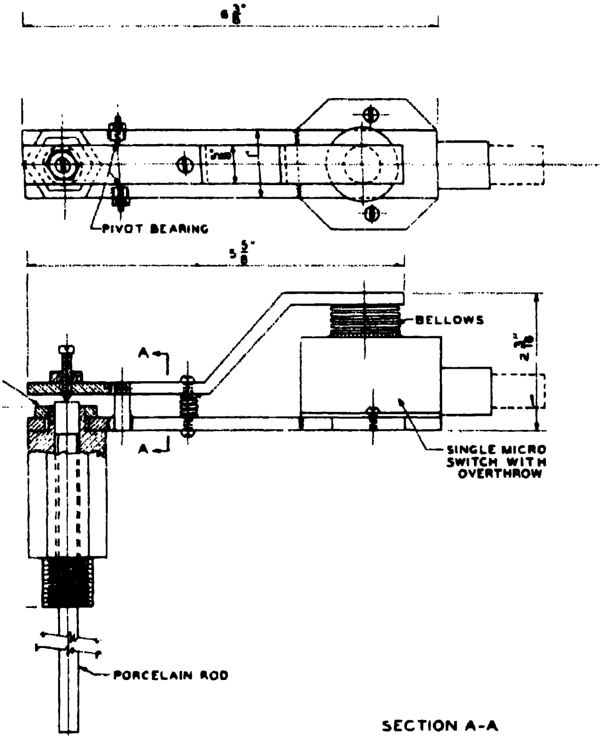

FIG. 2. Constant temperature control.

Construction and Mounting of the Metal Block

The size of the block is determined by the application. The outside of the block is usually cylindrical, of a diameter and length to fit standard heating elements. At least one inch of metal wall should be provided between the constant-temperature zone and the heating element. Also six inches should be allowed at each end for zones of decreasing temperature. Thus the diameter of the block should be at least the diameter of the constant-temperature zone desired plus two inches, and the length of the block should be the length of the desired constant-temperature zone plus twelve inches.

In determining the size of the block it is often desirable to consider making the thermostat adaptable to a number of uses rather than a single use. A convenient way of doing this is to make the size of the constant-temperature zone large enough

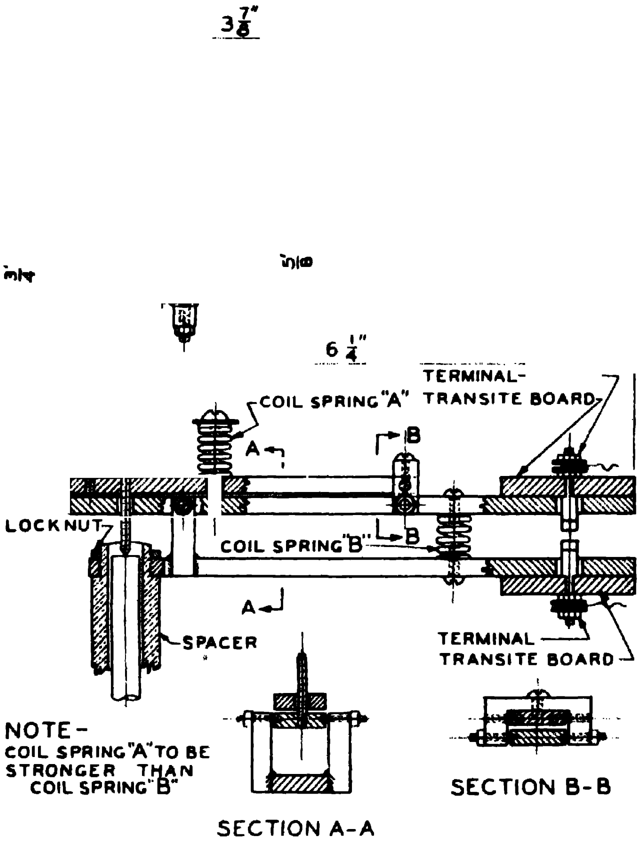

Fig. 3. Constant temperature control.

to accommodate the largest anticipated article, and then make a series of snug-fitting bushings to reduce the size of the constant-temperature zone for the smaller articles. In this way a single unit can be made quite flexible and can be made to serve a variety of purposes.

The temperature control mechanism is mounted on the wall of the metal block with the porcelain rod extending at least ten inches into the wall. Directly across from the hole drilled for the porcelain rod a similar hole is drilled for a thermometer or thermocouple. Other details of the machining of the block must be left to the individual user.

In Fig. 4 a vertical mounting for the block is shown. Although the block can be mounted and insulated to suit the individual user we have found this mounting most useful and able to withstand long and rough service. Most of the construction details and dimensions are given, although some of the dimensions are dependent on the size of the block and hence cannot be given. Once the size of the block is determined the missing dimensions can be determined from those given.

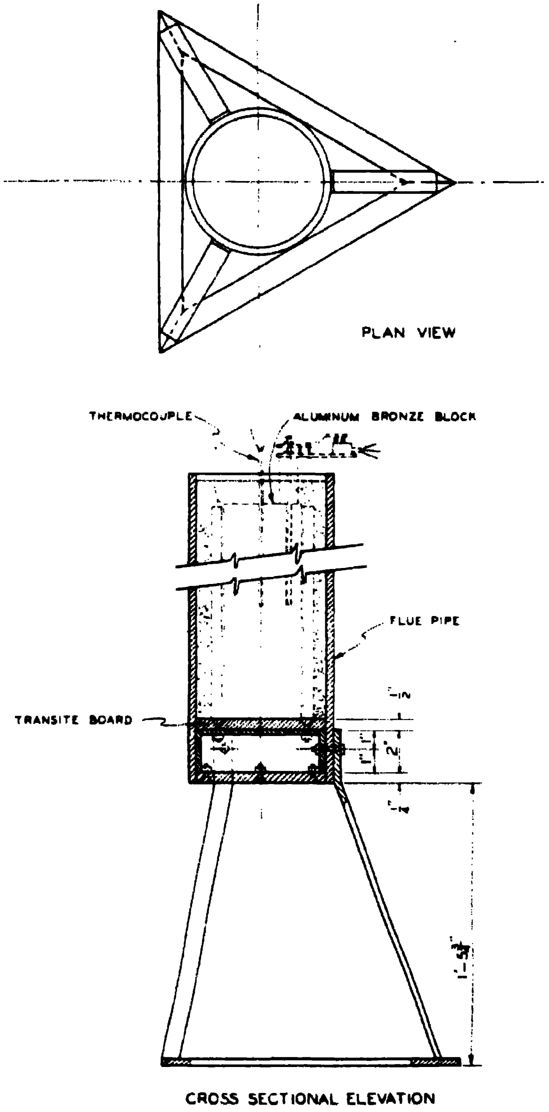

FIG. 4. High-temperature thermostat mounting.

A small panel board has been attached to the Transite tube which forms the exterior covering of the block. We use this panel for mounting the relay and a double-pole double throw switch. This switch is connected so that the block can be rapidly brought up to temperature on 220 volts and switched over to 110 volts for operation.

Operation and Performance

In a new unit it usually takes several hours (5-8) of rather close watching to get the temperature adjusted. This is apparently due to taking up slack in the temperature control mechanism. Often it will be found helpful to put a cone-shaped point on the bottom end of the porcelain rod so that the rod finds the deepest point in the drilled hole and stays there. After the preliminary adjustments the temperature remains constant. Over a period of 24 hours there is slight tendency to drift, although as a precaution the temperature should be read every hour to be certain that the device is functioning properly. A sticking relay is likely to result in damage to the metal block from overheating. A magnetically operated mercury switch is preferable as it is totally enclosed and eliminates the explosion hazard of open contacts.

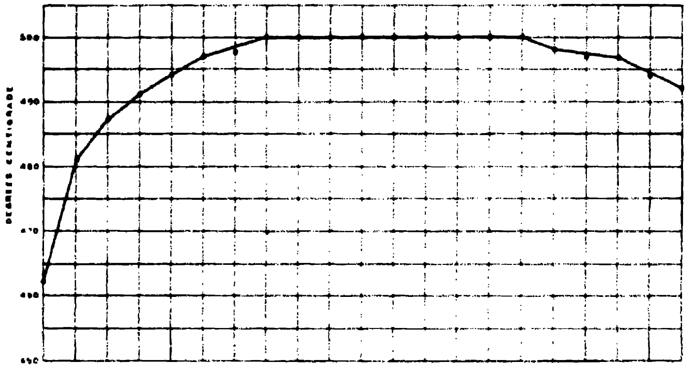

Fig. 5. Temperature distribution in aluminum bronze block, thermostat at 500 °C. (Block 4" × 24".)

The constant-temperature zone in the thermostat is constant so long as the temperature distribution of the block is not disturbed. Passing material through the zone or conducting a chemical reaction in the zone may change this distribution. Usually the changes are slight due to the large heat capacity of the block. Passing comparatively large amounts of material through the constant-temperature zone will displace its location in the direction of flow. In such cases, it is necessary to determine the location of the zone under the conditions of test.

As for the performance of these thermostated blocks, it is not convenient to give data for all temperature ranges. At 500 °C a 4"×24" block, constructed according to the principles described, gave the temperature distribution graphed in Fig. 5. As can be seen, the constant-temperature zone is a well developed plateau rather than the more or less rounded peak characteristic of most high-temperature devices.

At 500 °C the temperature controller will keep the temperature so nearly constant that no deviation is noticed with a thermocouple and potentiometer whose sensitivity is ± 1 °C at 500°.

Some of the Uses for the Thermostated Blocks

We have found these thermostated blocks very convenient in the study of the thermal and catalytic reactions of hydrocarbons. Where quantitative data on yields are necessary, it is imperative that the temperature of the reaction being studied be kept constant throughout the run. It is then possible to obtain results that can be duplicated. These thermostats also permit the more precise determination of the effect of temperature on the reactions being studied.

By way of illustration these thermostated blocks have been used in studying the pyrolysis of propane and butanes, the catalytic dehydrogenation of ethane, propane, butanes, butenes, the aromatization of various gasolines, the polymerization of olefin hydrocarbons, and the catalytic cracking of heavier hydrocarbons.

These devices are most convenient in cases where a reaction must be studied at elevated temperatures for long periods. Studying the useful life of catalysts is one such application. For example, we have used such a unit continuously for seven months at 500 °C without a shut-down for any reason whatever.

From the foregoing description, it can be seen that the thermostated block is a precision instrument for the temperatures indicated, and in cases where it can be used it is a useful and convenient tool.

A High-Speed Multiple-Temperature Recorder

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Introduction

In connection with the study of hardenability of steels, it was found desirable to determine experimentally the rapidly changing temperatures of several points in a specimen during the quenching process. Instruments for recording such transient temperatures occurring at a single point have been described in the literature,[1] but to the authors' knowledge no instrument has been developed which will record satisfactorily the temperatures of several such points simultaneously.

In view of the active interest in hardenability,[2] as well as other possible applications of such an instrument, the authors submit the following brief description of a high-speed multiple-temperature recorder which has proved satisfactory for recording temperature changes encountered in steel quenching.

Theory

The recording of rapidly changing temperatures occurring at several points in a test specimen is accomplished by a number of relatively simple pieces of equipment. Thermocouples are placed at the points in the specimen for which temperature records are desired. By means of a motor-driven selector switch, the thermocouples are connected one by one to a vacuum tube amplifier. Because of the relatively high impedance of the amplifier input circuit, the current drawn from the thermocouples is negligible. Measurements are therefore made of potential difference rather than of current. The amplified potential is impressed on the plates of a cathode-ray oscillograph, and the resulting deflections of the fluorescent spot recorded on a continuously moving photographic film.

A measured and fixed external potential of approximately the same magnitude as the maximum thermocouple voltage is fed into the selector switch at the end of each cycle, and appears on the photographic record as a comparison deflection. This eliminates absolute errors in the amplifier and oscillograph and makes the final results independent of the amplification factors.

Timing of the record is accomplished by driving the selector switch at a known constant speed, thereby making each cycle of deflections on the film equivalent to a definite interval of time.

Description of Apparatus

Thermocouples. The Chromel-Alumel welded junction thermocouples used are solidly peened into the specimen. Small-size wire is used to insure rapid response, to minimize heat conduction from the junction, and to facilitate placement. The wires of each Cr-Al pair are insulated throughout their length and are connected directly to the binding posts of the selector switch. Chromel-Alumel couples possess a voltage-temperature coefficient of approximately 22.5 microvolts per degree F and are satisfactory for the temperature range involved.

Selector Switch. The selector switch, Fig. 1, has a Bakelite commutator with two sets of slip-rings and contact buttons. A rotating arm carries spring-loaded brushes which connect between the stationary buttons and the slip-rings. A contact interval approximately 50 per cent longer than the thermocouple contact period is provided for the reference voltage, which is obtained from a built-in dry cell and slide-wire arrangement. One interval of approximately half of the thermocouple interval is left open to provide spacing of the cycles and to indicate the base line of the deflections. The first selector switch built used five thermocouples and was driven at three cycles per second, thus yielding 900 temperature readings per minute. This switch has been speeded up to 500 r. p. m. or over 8 cycles per second. At 500 r. p. m., which corresponds to 2500 temperature measurements per minute, the performance was found satisfactory. A new switch is being built providing for seven thermocouple connections and rotating five cycles per second, giving 2100 thermocouple readings per minute.

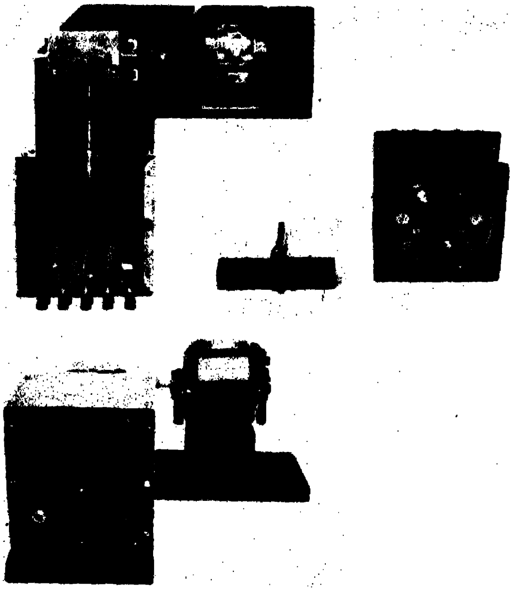

FIG. 1. Two views of selector switch assembly, with separate views of commutator and switch arm.

A hand selector switch and terminals are provided for measuring the potentials of the individual thermocouples and the reference voltage by means of a portable potentiometer. The selector switch assembly is mounted in a metal box which is grounded to minimize stray pickup.

Amplifier and Oscillograph. It is necessary to amplify the selected potentials in order to obtain voltages capable of operating the cathode-ray oscillograph. A special amplifier is used for this purpose, Fig. 2. The first stage is battery-operated, this arrangement eliminating an additional rectifier and reducing the a. c. interference. The operating point of the first tube is controlled by a dry cell and slide-wire adjustment of bias. The difference between the IR drop in the plate load resistor of the first tube and the plate voltage tap provides the grid potential for the second tube. Thus the operating points of both tubes depend on the bias

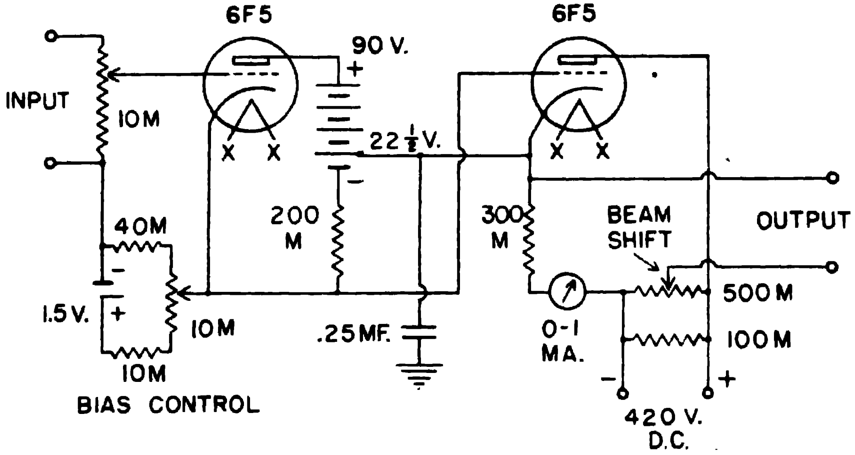

FIG. 2. Two-stage direct coupled voltage amplifier.

on the first tube. The circuit constants are so chosen that nearly straight-line amplification is obtained when a meter in the plate circuit of the second tube reads about 0.35 milliampere with no signal. A calibration curve of the amplifier is necessary for best results. A bucking voltage is provided to eliminate the no-signal

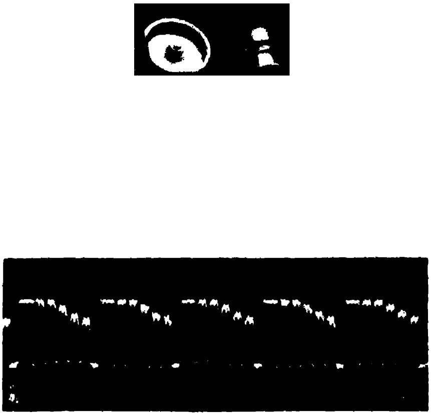

FIG. 3. Motor-driven camera and sample of record film.

potential across the output terminals, and to provide a means of shifting the base position of the spot on the oscillograph screen. The "B" power supply is conventional and includes very good filtering.

Connection is made directly from the amplifier to the electrostatic deflection plates of a commercial oscillograph. Thus the thermocouple potentials passing through the selector switch and amplifier are indicated in turn by vertical deflections on the oscillograph screen. Tests show that the time interval between the impression of a potential on the amplifier input and the positioning of the oscillograph spot at the full deflection appropriate to that potential is of the order of 1/300 second.

Camera. The shutterless motor-driven camera, Fig. 3, yields a continuous record. Ultra-sensitive 35-mm motion-picture film in daylight loading cartridges is used in conjunction with an f-3.5 lens. The film winding drum is equipped with a friction clutch and provision is made for rewinding the film into the daylight cartridge.

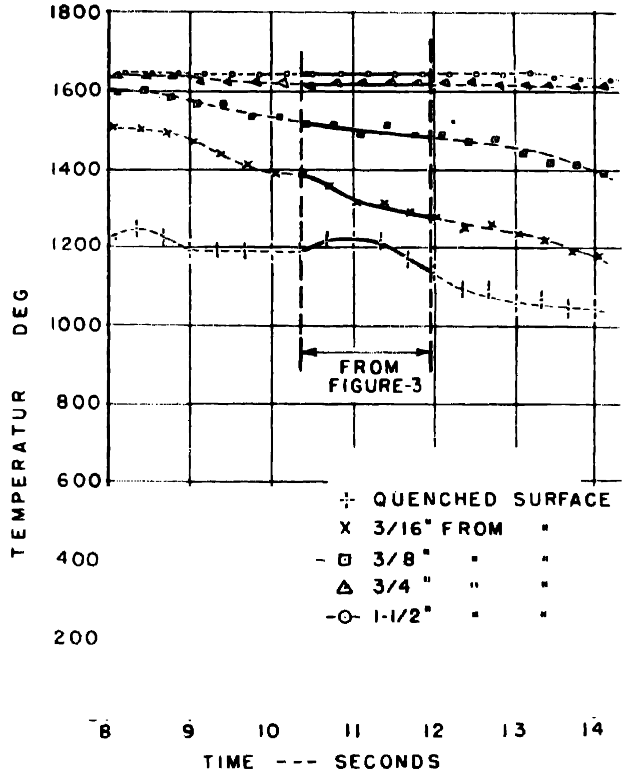

Fig. 4. Section of cooling curves for end-quenched steel specimen.

Reduction of Data

Measurements may be taken from the photographic record by projection and enlargement upon a screen or by other suitable means. A small amount of alternating current superimposed on the record is not a serious hindrance, though it would probably be desirable to eliminate it. A sample of film is shown in Fig. 3, and a plotted curve showing the experimental points is presented in Fig. 4.

Calibration and Accuracy

In calibrating the equipment, a series of known constant potentials was connected to the selector switch and a record of the corresponding oscillograph deflections made on film in the usual manner. A number of switch cycles were recorded and the mean deflection for each potential, as a percentage of the reference deflection, was plotted against the voltage of the input. See Fig. 5.

With an operating speed corresponding to 2500 temperature readings per minute, the maximum deviation from the mean for any potential was found equivalent to less than plus or minus 35 °F. For lower speeds this deviation was less.

Conclusion

The equipment described above has been found satisfactory for multiple-temperature recording in the investigation of steel quenching. A permanent record of a number of varying temperatures, with several hundred readings per minute on each, was obtained with an accuracy sufficient for most purposes.

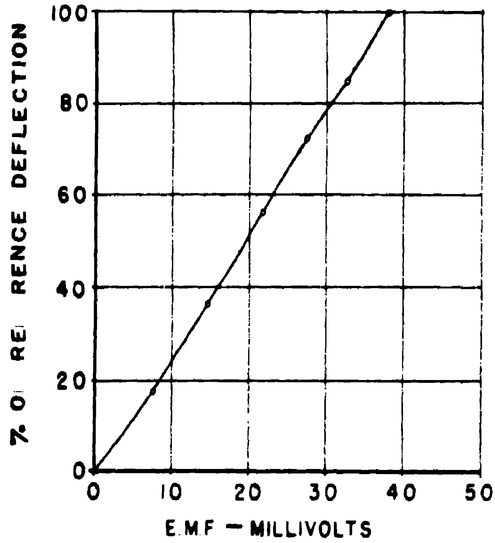

Fig. 5.

Calibration curve for reference potential of 38.0 mv (No-signal plate current = 0.35 ma).

Acknowledgment

The authors wish to express their sincere appreciation to Professors N. F. Ward and J. E. Dorn for their guidance and counsel, to Mr. F. A. Ryder for assistance in solving some of the electronic problems, and to Professor L. M. K. Boelter for his interest and encouragement. They also wish to thank the Department of Mechanical Engineering of the University of California for providing funds and facilities.

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Fast Single-Curve Recording of Multiple Thermocouple Measurements of Soil and Air Temperatures

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The work which we are to describe consists in the measurement, in rapid succession, of the temperatures at more than a hundred locations in a citrus grove, during nocturnal frosts. The conditions encountered are unfavorable for attaining the desired accuracy of ±0.5 F.

The California Agricultural Experiment Station has a project on frost protection of citrus orchards, aiming at a control of the smoke nuisance resulting from the occasional use of three million orchard heaters. Their use is based on empirical field practice which is so closely controlled in order to save fuel that occasionally the frost protection is inadequate.

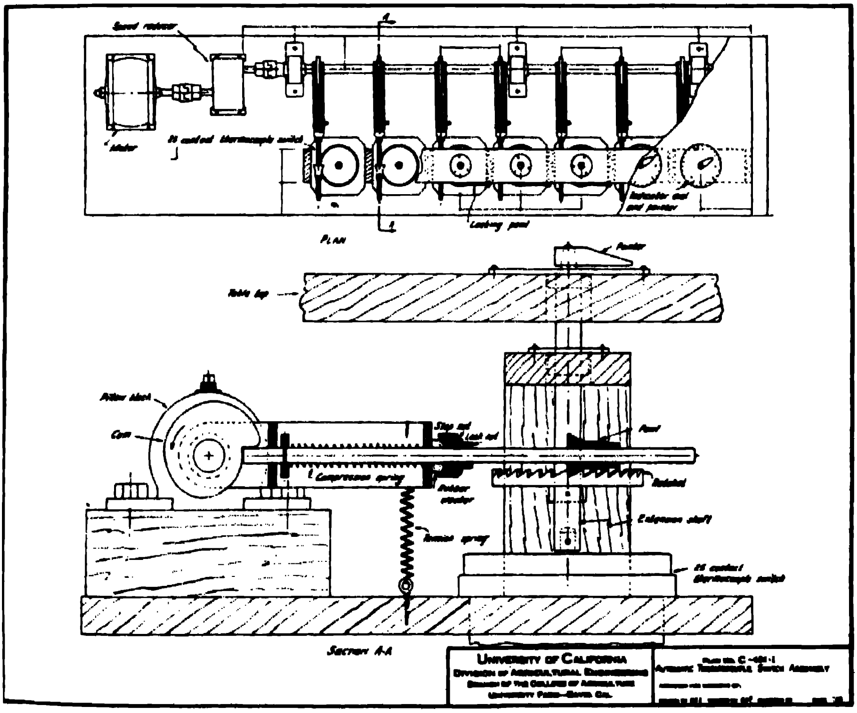

FIG. 1. Switch drive mechanism for connecting 175 thermocouples successively to a photoelectric potentiometer and single-pen recorder.

Mr. Floyd Young, Senior Meteorologist in charge of the Fruit Frost Service of the U. S. Weather Bureau (Pomona, California) made studies 20 years ago of orchard temperatures which showed that orchard heating is practical. He was forced to use thermographs and mercury thermometers in studying temperature distribution under very uncomfortable and inconvenient conditions.

In the first year of the present work, the program called for temperature observations at 160 stations at as frequent intervals as possible. We employed iron-constantan thermocouples, and conformed to best practice by providing a separate pair of leads for each thermocouple up to a reference-junction box, and to an individual pair of contacts in moisture-proof rotary switches. These were standard 24-point switches, which were driven by a cam-actuated spring pawl and ratchet, so that there was a quick shift and then a dwell for potentiometer balancing and recording (see Fig. 1.) The transfer of the recorder from one rotary switch to another was made through electric relay-operated mercury switches. The rotary switches were driven by a synchronous motor at such a speed as to switch from station to station every 7.5 seconds.

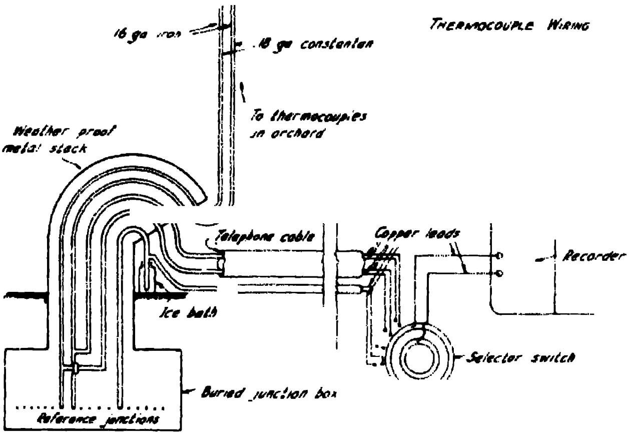

FIG. 2. Wiring diagram showing use of constant-temperature reference junctions in the field with copper leads to instruments.

A recording single-curve potentiometer was chosen instead of a multiple-point recorder because of the multiplicity of stations. Early difficulties with the recorder due to deterioration of relay contacts and spring fatigue were overcome by substituting a dual vacuum-tube control by which, electrically, the relays could be quickly adjusted separately. To avoid errors due to transient temperature gradients in the recorder, the built-in cold junction compensator was removed.

All the cold junctions were placed in a buried reference-junction box with copper leads to the selector switches as shown in Fig. 2. A thermocouple with one junction in an ice bath and the other in the reference-junction box was used to measure the temperature of the junction box. The pen of the recorder was set so that the ice-bath junction indicated 32 °F on the recorder.

The program for the second winter called for fewer stations, reducing the number of thermocouples to 75, and in some cases required more frequent recording. in order to follow rapid changes of temperature over a portion of the orchard due to local air eddies. A Weston Model 721 Photoelectric Potentiometer and a 5-10 milliampere Esterline-Angus Recorder were installed. Fig. 3 pictures the instrumentation in the field laboratory house. Fair records of 75 temperatures in 2 minutes could be made with this system (switching interval 1.6 seconds) but for temperature differences of less than 20 °F between successive stations, allowance had to be made for under-travel, and for larger differences, for over-travel. Another

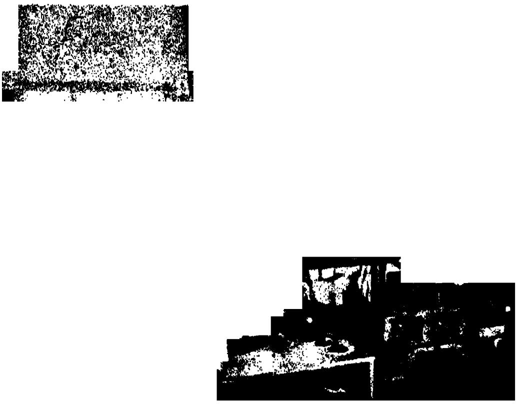

FIG. 3. Photograph of instruments and installation in orchard-heating field laboratory house.

practical difficulty with this fast recording was the excessive time required to analyze the voluminous data so obtained.

During the active periods of observation the Weston potentiometer was operated at $\frac{1}{8}$ the fast rate and gave very satisfactory readings of 75 temperatures on a 10-minute cycle (switching interval 8 seconds). In this case the transfer from one rotary switch to another was made through mechanically-driven brass commutators with brass brushes. No particular instrument trouble was experienced with either the Weston or the Esterline-Angus, but two minor peculiarities were noted. The null balance is not immediately established, and the temperature indication for distant thermocouples is slightly higher than for near-by couples. The latter indicates

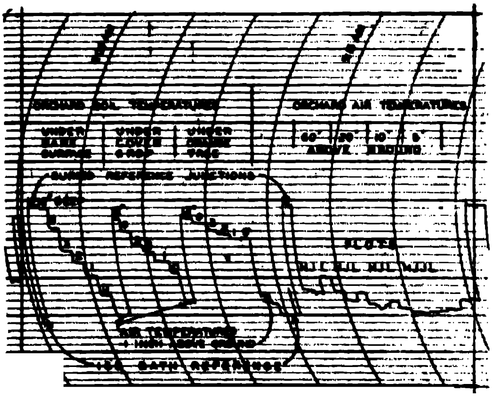

FIG. 4.

Sample of single-pen recorder chart indicating 50 different temperatures.

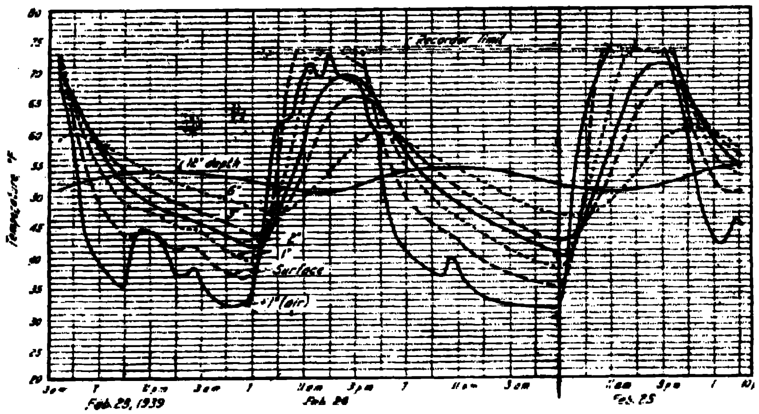

FIG. 5.

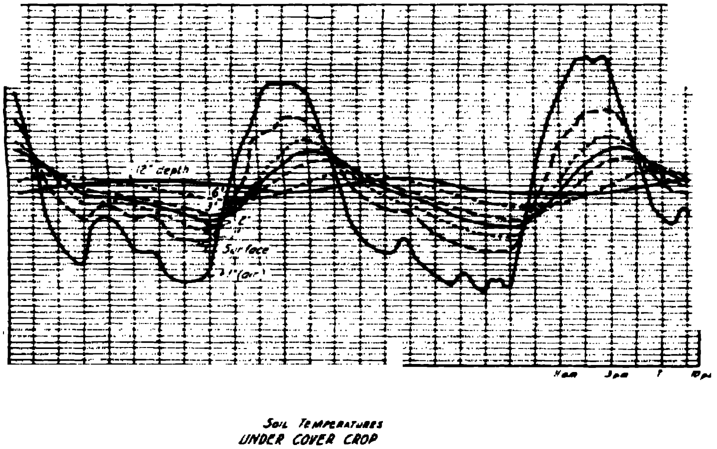

FIG. 6.

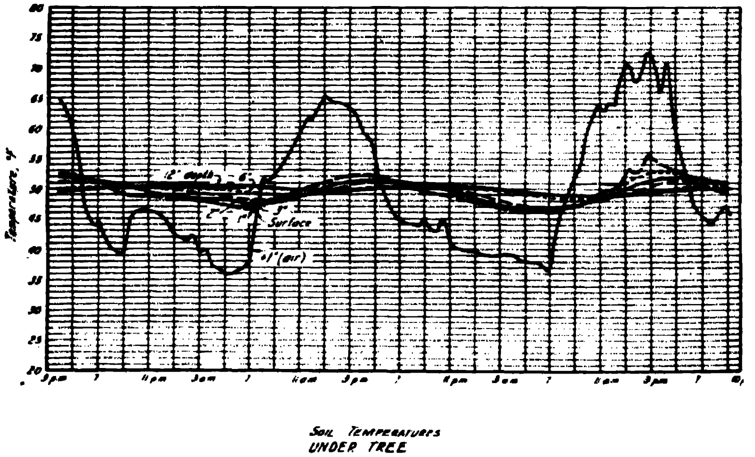

FIG. 7.

Readings of soil temperatures in 3 plots similar except for surface exposure. Fig. 5 is with bare surface; Fig. 6 with mustard cover crop; and Fig. 7 under young orange tree.

that for precise instrumentation with this equipment all couples should be given the same resistance.

Soil temperatures do not vary rapidly, and there are inactive periods when infrequent records of air temperatures are wanted. For these purposes a slow cycle of 50 temperatures in 30 minutes is used. Fig. 4 shows a good example of soil temperatures but a poor example of air temperatures because of the weak inversion at that particular time. The different soil temperature gradients for different surface exposures are striking, but for instrumentation it is more interesting to note the different lengths of dwell in the under-tree records for 6-, 3-, and 2-inch depths in spite of the mechanical timing. The ½ interval and 1½ for the ice-bath readings show the staggering of the pawl drive cams. The recorder pen is set by these ice-bath readings, and the back of the chart is used because the overall calibration (to the buried reference junctions) does not coincide with standard rulings. The chart is read in a roll holder equipped with celluloid sheets properly ruled for temperature and for switching interval.

The readings of a 54-hour run of soil temperatures are shown in Figs. 5, 6, and 7. The three series are in the same kind of soil close together but under a bare surface, under a cover crop of mustard, and under a 9-year old orange tree respectively. The air is colder than the ground because it is chilled by surrounding foliage which at night is cooled by radiation to a lower temperature than the ground.

High-Speed Temperature Measurement in Petroleum Refining

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During the past two years, the oil industry has been in one of the most active periods of development in its history. New catalytic processes are going into operation in increasing numbers. Alkylation, isomerization, dehydrogenation are becoming familiar terms to all refiners, and moreover all indications point to the adoption of catalytic cracking on a wide front in the near future. In general, these catalytic plants are of the intermittent type because periodic loss of catalyst activity makes regeneration necessary. This regeneration usually consists of the controlled combustion of carbonaceous material formed in the catalyst chambers.

In most processes involving C_4 fractions and lighter, the periods of operation and regeneration are long enough to permit simple hand operation. One or two standard speed six-point recording potentiometers are sufficient, with thermocouples placed at equal intervals throughout the catalyst bed to give a satisfactory picture of the progress of reactivation, since the zone of combustion in the catalyst moves in a period measured in hours. Catalytic cracking, on the other hand, introduces a much more complex problem. At the present stage of development, the regeneration period may be as short as 10 minutes, and during that interval much greater quantities of carbon must be burned than in the case of other processes. As a further complication, capacities and increased heats of reaction in catalytic cracking would indicate that the use of one large catalyst bed is not practical, since the accumulation of heat in the center of the bed may easily be so great as to injure the catalyst. This leads to modifications such as exchanger type reactors, in order that some temperature-regulating medium may be brought into contact with the catalyst bed.

As a further consideration, the complete cycle of a regenerative process of this sort is such that several separate catalyst chambers are necessary if intermittent heavy overloads on the utilities system are to be avoided.

One general method of accomplishing the reactivation is to circulate large quantities of flue gas in a closed system, adding air at the reactor inlet to introduce the necessary oxygen, the excess flue gas thus produced being released to the atmosphere by a back-pressure regulator. If we assume that the burning progresses evenly, and that the carbonaceous deposits are distributed uniformly throughout the catalyst bed, then the reactivation will reach completion just when the burning zone reaches the end of the catalyst bed. Immediately afterward, the circulating gas which had been leaving the reactor chamber substantially oxygen-free, will contain all the oxygen originally introduced, and unless cut down by hand adjustment an additional amount will be added before the flue gas re-enters the chamber. This condition is aggravated by the fact that the large volumes of circulating flue gas which are required to minimize temperature rise within the reactor make the cycle very short. Theoretically the increase in O_2 percentage would have no detrimental effect, since there is no combustible material present in the system; but at the temperature of circulation, a high concentration greatly increases the oxidation of the materials of construction, and for this reason alone it is undesirable. More seriously, however, the deposits in the catalyst bed are not necessarily uniform, nor do they burn on an even front. This can easily lead to the situation where a single section of a catalyst bed is completely burned out, thereby allowing a certain higher percentage of the O_2-bearing gas to circulate in the system. This will cause an increase in O_2 content similar to the hypothetical case, but in a lesser degree. It can very quickly, however, build such a concentration that the unburned part of the catalyst bed may develop temperature ruinous to the catalyst and in extreme cases to the process equipment itself.

In view of this it becomes essential that the temperature conditions within the catalyst chamber be closely observed, and this is best accomplished by recording a selected number of points by means of a potentiometer pyrometer. If we assume that regeneration is complete in 10 minutes, a standard speed six-point recorder printing every 30 seconds would record each temperature only three times. It is apparent that under these conditions very little information can be derived from such a record, since the essential information desired is the magnitude of the peak temperature and the time at which this peak is reached. One might say at first glance that a group of single-point recording instruments will give a more complete story since they are limited only by the response of the primary element, but in the case outlined which may involve more than fifty points, this expedient is not economically sound.

The standard recording potentiometers available today are in general constructed very conservatively, and are designed for a good many years of operation with an absolute minimum of attention. When confronted with the problem of increased speed, manufacturers have tried to determine how much the standard models could be speeded up without sacrificing reliability. By careful consideration of all the factors in each case, such as range coverage desired, type of couple, length and gage of lead wire, etc., it is possible to speed up some of the present recorders about two to ten times. This is accomplished by alterations of the galvanometer sensitivity, circuit resistance, and motor speed. It seems reasonable to assume that this point marks the practical limit of development along these lines, since, for one thing, on most standard instruments the galvanometer must support a long horizontal pointer, thus making the period of the galvanometer the limiting factor.

The fastest standard instrument available is one that makes use of a photoelectric cell and a light ray which is reflected from a small mirror near the axis of support. This construction allows the use of a more sensitive short-period galvanometer and the recorder includes a unique system of counter emf which tends to minimize any tendency for cycling.

Also, the instrument is designed to print immediately after having been in substantial balance for a fixed number of seconds, so that if successive temperature records are very close together, the printing interval is very short. Unfortunately in many catalytic processes, at a time when the record is most vital, the temperature points are from the nature of the process more widely spaced, and this particular advantage is to a certain extent, if not completely, nullified. An interesting limitation of this instrument is the fact that, should the instrument try to follow a temperature fluctuating at the high rate of more than $\frac{1}{8}$ of the scale range (*e.g.*, $\frac{1}{8}$ of 1000°) per minute, it will fail to remain in balance long enough to cause the printing mechanism to function; thus the indicating pointer might follow the temperature quite closely, yet never print a single record.

On the other hand, it must be borne in mind that the increased printing rate must of necessity be accompanied by some increase in maintenance, per instrument, and where several instruments are involved this may become a decisive factor.

In a number of units in operation or under construction at the present time, an analysis similar to the foregoing has led to the selection of the six-point recorder as most nearly meeting the demands of the industry. With a 5-second printing interval, this gives a 30-second time cycle. At first glance this would seem to entail no particular problem with regard to the primary element, but one must remember that final selection of the instrument was a compromise and that the primary element should be able to respond to rapid temperature fluctuations. At the high temperatures encountered (900 to 1500 °F) it is difficult to design a protecting well mechanically and thermally suitable. It is true that a thermocouple will respond very rapidly to temperature fluctuations if:

(1) A small-gage wire such as No. 24 be used;

(2) A sensitive couple such as iron constantan is used;

(3) The couple is firmly in contact with the bottom of a well of small diameter; and

(4) The well is inserted directly into the stream of regenerating gas.

The first three of these four conditions are almost impossible, and the fourth extremely difficult to fulfill. Oxidation at the high temperature makes the No. 24-gage couple impractical, and also precludes the use of iron and constantan wires, since the iron wire will not stand up satisfactorily under these conditions. It is essential that great care be taken in inserting the couple to insure good contact of the hot junction with the well, and if it is possible to weld the thermocouple to the well, the utmost speed of response is obtained. The physical structure of the reactor chamber in general makes it necessary to use a long well which must be quite heavily constructed.

The well may be constructed of 18-8 stainless steel, although as a general rule straight high-chromium alloys are more stable over a wide range of temperatures. Fortunately most of the stainless alloys are better heat conductors at high temperatures than at low, so that no complications are introduced from this source.

As yet we have not discussed the value of the record obtained by these high speed instruments. Primarily they are useful as an operating guide for the purpose of determining how much air should be admitted to the system. If, however, we are to encounter temperatures fluctuating so rapidly as to necessitate such instruments, is the plant operator going to be able to correct the system quickly enough? Bearing in mind the unavoidable lag in the system, however short it may be, and that of the operator, it becomes doubtful that the record can be more than the roughest guide in this respect. From the standpoint of acting as an indicator of the condition of the catalyst throughout the bed, an analysis of the record can be very valuable. This might be said, however, to be of interest to the industry, primarily in the development stage, and it is very probable that this need will diminish as the processes are brought to a more advanced state.

This point is a most interesting one, since it brings up a question which, although universal in scope, is very well illustrated by the case in hand. Let us assume that a new company enters the field with a catalytic process that leads to a design incorporating a regeneration system similar to those at present under design or in operation. The company approaches the instrument manufacturer with regard to the problem of recording a good many temperatures within the catalyst bed, and is presented with data worked up for the instruments which they already have in operation. The manufacturer will in all probability point out that they are interested in supplying the needs of the industry, but they have absolutely nothing to do with the development of high-speed recording. What is actually required is much closer coöperation between the manufacturer and the design engineers. Unfortunately a considerable period of time passes between the design of a plant and the point of actual operation where reasonable conclusions may be drawn as to the actual value of some questionable piece of equipment. In the meantime several plants are under construction and there is serious danger that the items in question become a permanent feature of the process. This does not imply that the temperature records are unnecessary, but there is a serious question as to whether the design engineer and the manufacturer are meeting at the optimum point.

The extreme speed, from ten to fifteen times faster than the fastest mechanically actuated pyrometer, is accomplished by electronic means in one instrument nearly five times as costly as the standard potentiometer, and another about twice as costly. However, these instruments are not adaptable to multipoint service at the present time.

Upon thorough investigation of the equipment offered, it is apparent that the practical maximum printing speed is very close to four seconds per thermocouple point, regardless of the make. Even at these speeds in most cases careful consideration must be given to the thermocouple installation. No fixed time cycle instrument is available which will cover the full chart range at this speed, even though a wide range is specified in order to increase the galvanometer sensitivity. In fact, the range coverage may not exceed 20 per cent of the scale range in some instances, even though the resistance of the external circuit is kept to the minimum. It does not seem plausible that any immediate developments will bring about a material decrease in this time.

The basic requirement is not necessarily best met with any of the available equipment. If we are interested in observing the progress of reactivation by observing the temperature rise in the catalyst bed, it is apparent that an arrangement that records the maximum temperature of a group of several thermocouples with an indicating device to show which couple is recording would serve very well as a guide for process control. No instrument capable of this action is available in the potentiometric field, but multiple-bulb vapor-tension type systems function to indicate maximum temperature, and there is little doubt that an electric instrument could be devised if there were a real demand. As a matter of fact, an instrument of this type could be used directly as a controller actuating a control valve in the makeup air line to the system. We do not suggest that such a system represents a perfect solution, but it is certainly one on which a good deal of work could be done to the mutual benefit of both supplier and consumer. The progress of the industry depends on constant consideration and investigation of new methods.

In the present case, for example, let us assume that a change in design entirely wipes out the demand for high-speed recording in the petroleum industry. The development work done is almost certain to find application in some other field. Take, for example, the recorder mentioned previously. This instrument is now available with a fixed printing interval of 30 seconds, but is convertible at the flip of a switch to variable time cycle high-speed recording. Thus if the temperatures are regulated by hand control, this switch is a convenient means for establishing the trend of temperature after readjusting the system for changing conditions.

Conclusion

The following summary represents the conclusions to be drawn with regard to the progress and needs of the petroleum industry for high-speed temperature recording:

(1) Potentiometric recorders are available with a minimum printing interval of about four seconds.

(2) Higher speeds are available at greatly increased cost for single-point records only.

(3) Although several plants in operation are equipped with high-speed recorders, it is felt that the trend will be toward the elimination of these instruments in favor of a device which records and controls the essential temperature in a group of several thermocouples.

(4) Closer coöperation between the manufacturers and the users will bring about a satisfactory solution of this problem.

Performance Characteristics of Recording Potentiometers

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An ideal recording potentiometer might be described as one that will accurately record all changes of the measured electromotive force without hesitation or instability. In practice however, one finds neither absolute accuracy, instantaneous action nor complete stability under all conditions. Moreover, the performance of the many available recorders varies so widely as to make it necessary in some cases to select a particular type. It is important, therefore, that one be able to analyze recorder performance in terms of clearly definable and measurable characteristics.

A typical recording potentiometer has a measuring circuit including a conventional slide-wire, and some means for balancing emfs, each being a unique combination of electrical or mechanical devices. A galvanometer connected in series with the measured emf indicates by its non-deflection that the slide-wire emf at a particular contact position is balanced against the measured emf. The battery current flowing through the slide-wire (and thereby the accuracy) is kept within prescribed limits by periodically balancing the voltage drop through a part of the potentiometer circuit against the voltage of a standard cell.

The means for balancing emfs must detect any deflection to which the galvanometer may be forced and must then move the recording pen and the contact brush of the potentiometer slide-wire toward a new position until the galvanometer is no longer deflected.

Recording Sequence

The sequence of action involved in each recording performance will usually assume the following order:

(1) The measured emf changes and causes a galvanometer deflection.
(2) The balancing means detects this deflection and starts the recording pen and the slide-wire contact brush toward a new balance.
(3) As the new balance is approached the deflection of the galvanometer decreases.
(4) The return of the galvanometer restores the balancing means to inactivity and stops the pen and contact brush.

The time required for this complete cycle varies from about one second to over one minute in the various types of commercial recorders, and is in general dependent not only on the inherent limitations of a particular balancing system but also on the limitations imposed by industrial requirements.

Balancing Means

The various recorders differ principally in their balancing means. Two general types are available, the one mechanical and the other electrical. In the former, an extended pointer attached to the galvanometer coil reaches out between mechanical parts which periodically close and open on the pointer, say every two seconds or more. When the galvanometer is sensibly undeflected, that is, within a so-called "dead zone," the parts close and open without other action. When the galvanometer is sufficiently deflected, however, these parts, in closing on the deflected pointer, actuate some other mechanism for moving the pen and the slide-wire contact in steps toward the new balance. This mechanism usually includes an electric motor as the power source. When released, the galvanometer pointer swings toward its null position and the process is repeated until the galvanometer is no longer deflected. This periodic action of the balancing means is a characteristic of the mechanical instruments.

The principal electrical means for balancing includes two relays in the anode circuit of a triode amplifier, a lamp, and a phototube which is so connected to the grid of the triode that an increase of illumination increases the anode current. A focused beam of light directed onto a mirror mounted with the galvanometer coil is reflected toward the phototube behind a "controlling edge." In the balanced position a narrow image of the lamp filament is split by this control edge so that the illumination and anode current just suffice to maintain one relay closed and the second relay open, the difference between the opening current of one and the closing current of the other corresponding to the "dead zone" of relay inactivity. With the relays so held, the motor stops in the balanced position, but drives the carriage continuously upscale when both the relays are open, or downscale when both are closed.[1]

Carriage Traverse Time

The carriage speed and the time required for the carriage and pen to traverse part of the width of the chart to a new balance are important characteristics of these instruments. In the mechanical instruments this speed is a maximum when the galvanometer is fully deflected, and for lesser deflections it is proportional to the deflection. It is evident then that whatever affects galvanometer sensitivity, *i. e.*, the magnitude of its deflections, will affect the speed.

For example, suppose that the carriage is driven in steps occurring every 3 seconds, and that a maximum deflection of the galvanometer results in steps 1½" long. Under these circumstances the carriage would traverse a 10"-chart in 7 steps, requiring 21 seconds if maximum deflections continued. Actually the deflections decrease as the balance point is approached, so that considerably more than 21 seconds is normally required to reach balance, unless the last major step accurately corresponds to the deflection.

Suppose that near one end of the scale, 1 millivolt, for example, causes a galvanometer deflection corresponding to a step of one inch. At the middle of the slide-wire this deflection would be less in some types of recorders, because the effective resistance of the shunted slide-wire in series with the galvanometer increases to a maximum at that point, the step length being reduced perhaps to ¾". Thus more steps may be required to reach a balance at the middle of the scale because the last few are shorter. The effect is most pronounced with low-resistance galvanometer circuits.

In the electrically balanced instrument, the carriage travels at a constant speed practically independent of the magnitude of the galvanometer deflection. At the end of a long run the carriage stops substantially at the balance point and reaches exact balance after a few short steps, which decrease progressively. For example, the carriage might traverse a 10"-chart in 10 seconds and reach exact balance in a few seconds more.

Limitations of Balancing

There are severe speed limitations in the combined function of the measuring and balancing means. For example, galvanometers must be suitably damped, sensitive, and rugged. Inertia is unavoidable, and in general the undamped galvanometer periods range from about 2 seconds or more for mechanical recorders to about $\frac{3}{4}$ second or more for the electrical recorder. These characteristics have the effect of delaying the motion of the galvanometer during a balancing operation, primarily because of the inertia which delays a start, and because an opposing emf is induced in the moving coil. Now when the deflection is large and the carriage has begun to travel toward a new balance, it is evident that the carriage will continue to travel until the galvanometer returns to zero. But the galvanometer lags behind the contact carriage for the reasons given above, and in a simple fast system it will overrun the new balance point before the galvanometer can reach its zero. Furthermore, the galvanometer will swing beyond the balance point both because of its momentum and because of the overrun contact position. Consequently, the system will continuously oscillate about the balance point. This hunting will be the normal result unless the speed of balancing is very low or the dead zone (and the inaccuracy) very large, or finally, unless unique methods are introduced to correct for the out-of-phase relation between the balancing means and the galvanometer.

Dead Zone

An important characteristic of measuring instruments in general relates to the so-called "dead zone," variously called zone of insensitivity, or zone of inactivity. If a fixed emf is applied to a recorder, and the recording carriage is allowed to approach the balance point *very slowly* (by retarding the motion of the carriage) first from one direction and then from the other, it will be found that the two records obtained do not coincide exactly, but are displaced by an amount $2\Delta T$. The same result might be obtained by slowly increasing and then decreasing an emf in the thermocouple circuit to determine the increment of voltage necessary to just begin to move the pen upscale and downscale. These tests determine the dead zone or the maximum error, ΔT (from the one cause only), of recording at that point. Other points along the slide-wire may show different values of the dead zone, since the effective resistance in series with the galvanometer may vary as mentioned in the discussion of carriage speed.

We have described the dead zone that is effective when the measured emf is constant or when sufficient time is allowed for the galvanometer to deflect and the balancing means to respond. However, when the applied emf changes rapidly, the carriage may not respond until the emf is well beyond the limits of the dead zone, due to the inherent delays of the system. Although a more sensitive galvanometer would decrease the dead zone, any accompanying increase of its inertia or damping would increase the delay in response to a varying emf.

The effective dead zone is dependent further on back-lash and other errors of coupling somewhere between the recording stylus and the primary element of the driving mechanism.

It was pointed out that in general greater carriage speed may be obtained at the expense of a larger dead zone. For example, one electrical instrument has a carriage traverse time of 20 seconds with a dead zone of 15 microvolts (full range 10 mv). In a modification of the same instrument the carriage traverses the chart in 2 seconds and the dead zone is about 80 microvolts, while still another modification requires slowing the traverse to about 7 minutes in order to reduce the dead zone to 2 microvolts (full range 1.4 mv).

The dead zone may be expressed in terms of emf ($2\Delta e$), in temperature ($2\Delta T$), as a dimensionless fraction of the total range of the instrument $\left(\frac{2\Delta T}{(T_{\max}-T_{\min})}\right)$, or as a fraction of the measured temperature $\left(\frac{2\Delta T}{T}\right)$. Expressed as a fraction of the range the dead zone increases as the range is made low or "open."

It is well to point out that the performance characteristics of a recorder may vary, depending on any unique combination of its design characteristics and the conditions under which it is used. For instance, a recorder may behave erratically and give the largest errors of recording for a particular rate of change of temperature, or for a particular type or frequency of vibration. Also, the behavior may be different in following a rising temperature from that in following a falling temperature.

Another factor affecting the magnitude of the dead zone is the number of turns per inch of the helical slide-wire. The minimum error of recording cannot always be less than the potential drop across one turn of the helix. It might seem that the use of more turns per inch would necessarily decrease this error, but this will result only if there is sufficient sensitivity otherwise available, and enough to allow for the accompanying increase in resistance.

Standardizing

As was pointed out previously, it is necessary to compare periodically the voltage drop through a part of the potentiometer with the voltage of a standard cell, and to adjust the battery current accordingly. For most purposes this check is needed but twice a week, and much less often when the newer type of primary air-cells is used. The check is usually made by hand, but some makers have incorporated automatic standardization in their recorders. This type is useful where the instruments are inaccessible for long periods. One company uses periodic automatic recording of the standard current with a scale, by means of which a correction for a change in this current may be applied to the temperature records. The modern standard cell generally develops an accumulative error of about 0.01 per cent of its voltage per year.

Galvanometer Drift

A source of error may be found in a shift of the galvanometer zero, caused either by a permanent change of the parts under tension or by periodic variations resulting from ambient temperature changes. The effect of this zero shift can become particularly important where the dead zone is only a few microvolts. Otherwise it is seldom noticeable as the source of significant errors.

Reference Junction Compensation

General practice in the use of temperature-measuring potentiometers is to connect the thermocouple to the instrument with special extension leads so that the instrument temperature becomes the reference junction temperature of the couple. Any change in the reference junction emf corresponding to a change of instrument temperature is then automatically compensated by a change in the *IR* drop in a pure nickel resistor in one branch of the bridge circuit, placed near the reference junctions. The compensation can be made fairly exact (within 0.2 °F) for a temperature variation of about 50 °F, but less so for larger variations because of the difference between second order temperature coefficients of the couple emf and nickel resistance. When the surfaces of an instrument have different temperatures, internal temperature gradients are developed and compensation errors are likely to creep in. These errors may most easily be measured by observing the temperature of melting ice while subjecting the instrument to various draft and heating conditions. The problem of exact compensation becomes most acute for low range instruments, say below 200 °F, where one degree is a relatively large fractional part. Because greater and greater accuracy and lower ranges are constantly being demanded by industry, particular attention must be paid to the problem of exact compensation.

Sensitivity to Vibration

Recorders are subject to two general types of vibration: a relatively high-frequency, low-amplitude vibration, as from electric motors and turbines, and sudden shocks, as from forge hammers. The usual effect of the vibration on an unprotected instrument is to start the galvanometer oscillating and thus occasionally start undesirable carriage motion. This motion is particularly troublesome if there is asymmetry of oscillation of the galvanometer or of the balancing means, because in such case, as the galvanometer oscillates, the recovery of the balance is not complete after each step of the carriage and the algebraic sum of the departures is not zero. Another effect of vibration is to decrease the dead zone; but in spite of this, errors of recording are likely to increase. The ill effects can be considerably reduced by overdamping the galvanometer and designing its moving coil so that the center of percussion is near the center of gravity. It must be remembered that the usual galvanometer damping by induction retards rotation of the coil about the vertical axis only, and it may precess or otherwise move eccentrically about another axis if the natural period of the coil is near to that of the vibration frequency. Too much damping will cause undue lag in the galvanometer response and has to be avoided in instruments designed for high-speed recording. One aid in reducing the vibration effects is damping the balancing means so that rapid motion of the galvanometer is not detected; but this requires a short-period galvanometer and the scheme is limited to a few designs.

Multiple-point Recording

Instruments that record the temperatures of 12 or more different thermocouples are available and have a number of unique characteristics. In these recorders the couples are successively and automatically connected through a multiple switch to the potentiometer circuit as each record is printed. The interval between records is particularly important because the successive recording of the temperature of any one couple must be sufficiently frequent to reveal the continuity of temperature variations with the required accuracy. In general, it is unwise to select an instrument that is much faster or much more accurate than required for any particular application, because of the consequent unnecessary wear of parts of the instrument.

Inasmuch as the records are usually printed only after exact balance is reached, it is evident that overstepping and returning of the carriage to the balance point is unimportant except as it aids or retards fast and dependable printing.

The records may be randomly scattered over the entire range, and the carriage may have to traverse part of the chart repeatedly in the course of a complete cycle. The speed of printing can be expressed as the interval required for the carriage to traverse the chart plus that required for printing, or as the average interval of a large number of records.

It is desirable that the carriage come to an accurate balance and then print after a minimum interval, and in case the temperature is changing fairly rapidly it is important that the interval be particularly short. There is a maximum rate of temperature change that some types of instrument will cope with and print without excessive delay or error, for example, a rate of one-fifth of the range per minute, corresponding to 200 °/min for a 1000 ° range.

A changing temperature will introduce additional errors which combine with ordinary inaccuracies of recording. Those errors will in general increase directly with the rate of change of the temperature, and in a group of different instruments will be proportional to the lag or stepping interval of each instrument. Thus, if the temperature is changing at a rate of 20° per minute, a stepping interval of 3 seconds will be likely to introduce an additional error of about 1°.

The effects of vibration are in some respects apparently not as severe in multiple-point recorders as in single-point instruments, in that the record is not continuous; but in the mechanical type a sudden large deflection of the galvanometer may cause a large movement of the carriage and erratic printing.

The speed of printing can be increased considerably by the designer if the dead zone is proportionately increased, as was pointed out for the single-point instruments. For example, one standard electrical recorder will complete a cycle of 6 records (distributed over 2½ inches or a quarter of the chart width) in about 60 seconds, with an accuracy of ±0.1 per cent. A modification of this same instrument prints the 6 records in about 25 seconds, while the maximum error reaches ±0.4 per cent. As the need for faster multiple recorders has increased, with few exceptions faster printing in the various types has been obtained at the expense of needed accuracy. Most mechanical recorders are arranged to record after a fixed number of stepping intervals, in which case vibration effects and temperature changes during the last interval would seem to require particular attention. Also, if high-speed recording is attempted with these, the distance between records may not exceed certain limits if random printing is to be avoided.

The terminal boards of multiple-point recorders must accommodate many thermocouples and the problem of automatic reference junction compensation requires special attention. The entire set of terminals must have the same temperature to prevent errors due to temperature gradients in thermoelectric circuits.

Chart Speeds and Legibility of Records

The printed records must be clear and easily read. In multiple-point recorders, the records frequently intermingle and cross; hence satisfactory color schemes or numbers, or both, must be provided. The style of type must be such as to be read clearly, and it should be possible to estimate the center of the number or symbol with the accuracy required.

The chart of a multiple recorder must travel fast enough to indicate temperature changes clearly and to separate the numbers or symbols sufficiently. For example, if the numbers are 3/32" high, and in a fast recorder a cycle of 6 records is completed in 30 seconds, the chart speed must be almost 12 inches per hour to provide non-overlapping printing if the six temperatures are all appreciably different. If the temperatures are almost all the same the corresponding speed is almost 72" per hour. Fortunately, considerable overlapping can be tolerated without loss of legibility.

Calibration

Of course the performance of a recorder, so far as accuracy is concerned, depends fundamentally on the accuracy of the original calibration. However, this bare statement is not sufficient. The recorder is calibrated originally simply as an electrical instrument, the measurements being readily carried out with the required accuracy. Most industrial recorders are used with charts printed to read temperature directly; hence the accuracy of reading will depend on the accruacy with which the temperature lines are printed on the chart. Also it will depend on the reproducibility of the thermoelectric properties of thermocouples and the basic fitness of the thermoelectric data used to determine the dimensions of the printed chart. These dimensions are calculated for a uniform slide-wire, and the general practice is not to alter this uniformity to fit standard temperature-emf tables. Now, studies have shown that different thermocouples of the same kind, in general show nearly linear departures from standard tables. A little thought will reveal that if the standard tables are correctly set up, then in special cases a recorder can be calibrated to fit very accurately a single thermocouple; but if the original data are incorrect the resulting errors will reside permanently in the printed charts. Added to all this is the error caused by expansion of the chart paper with moisture content.

Sensitivity to Inattention

To be useful, recorders must be dependable, and particularly so when skilled maintenance is not available. A broken couple must not result in injury to the instrument, nor prevent the printing of temperatures of other couples in the case of the multiple-point recorders. Nor when control devices are added to a single-point recorder may it allow the controlled device to run amuck. Motors and moving parts must be oiled, but the frequency of oiling must not be critical. The requirement for periodic adjustments should be reduced to the minimum, and made non-critical. The pen or printing device must continue to provide clear records for extended periods. Dust found in ordinary industrial atmospheres ought not to cause untoward effects, and atmospheric moisture must not cause too much electrical leakage. However, it is good practice to keep recorders clean and dry.

Sensitivity to Wear

Finally, we might consider the effect of wear on instrument performance. The wear of slide-wires will introduce calibration errors and contact difficulties unless compensating provision is made. When back-lash of moving parts is found between the contact brush and the pen, increase of the dead zone with wear must be prevented. Wear in the mechanism connecting the galvanomter and the balancing means of the mechanical instruments is a separate consideration. In electrical instruments long, continuous operation of lamp, amplifier and phototube must be provided. In all instruments switch leaves and contacts must not be subjected to overload beyond their capacity, nor to appreciable wear. Clutches and friction drives must be designed for long use. Electrical insulation must be retained with age and despite a measure of abuse.

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Chapter 8

Special Applications and Methods

Thermometry in Hygrometric Measurements

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Aside from various types of pollution, the condition of the atmosphere is determined by the temperature and the amount of moisture which it contains. The latter can be *measured* accurately by *absorbing physically or chemically the amount of water in the form of vapor present in a given volume,* except when the quantity of water vapor is very low. Under the latter condition, the water occluded upon the walls of the measuring apparatus may cause serious error. A modification of the absorption method consists in measurement of the vapor pressure exerted by the water vapor rather than of its mass. In any case the equipment necessary is somewhat elaborate and expensive and the procedure requires time and very exact observations. A common empirical method of measuring the water content is to measure the *change in length of a hygroscopic substance,* such as hair. Instruments of this type must be calibrated by an absolute method; and as the physical and chemical characteristics of all hygroscopic substances are subject to change, frequent recalibration is necessary. Some materials show changes in optical and electrical properties depending upon the amount of water in the surrounding air, but none has proved reasonably satisfactory as a basis for measuring the humidity. The most accurate absolute method for determining the moisture content in the air is a determination of the *dew point, i.e.,* the highest temperature at which the water vapor present in the air is sufficient to give saturation. From a table of the amount of water vapor required to saturate the air at different temperatures, the maximum amount of moisture at the dew point is read off, and thus the actual water vapor content of the air is determined. In its most accurate form the *dew point hygrometer* consists of a thin plate of highly polished metal on the rear side of which a cooling liquid flows. The temperature of the liquid is varied until moisture in the form of a film of water or ice appears upon the polished surface. In the most accurate instruments the temperature is observed by means of a thermocouple junction soldered immediately behind the polished surface. The polished surface is observed with a long-focus microscope, and the temperature of the flowing liquid varied between appearance and disappearance of the film and the average of the observed temperatures gives the dew point with high accuracy.[1]

A much more common semi-absolute method is that of the *wet and dry bulb hygrometer.* In contrast to the dew-point instrument, from the temperature of which can be found directly from tables the actual water vapor present or the *absolute humidity,* the wet and dry bulb instrument, from the temperatures and a semi-empirical formula, gives the *relative humidity* or the fraction to which the air is saturated with moisture. Obviously, the relative humidity can also be calculated from an observation of the dew point, and the air temperature by dividing the amount of water vapor as obtained from tables for saturation at the dew point by the amount required for saturation at the actual air temperature; and similarly the absolute humidity can be found from the relative humidity. In meteorology, the relative humidity is usually defined as the ratio of the mass of water vapor actually present in unit volume to that contained in a unit volume when the atmosphere is saturated; in the other sciences, as the ratio of the corresponding pressures of saturated water vapor. (The ratios are usually multiplied by 100 and expressed as percentages.) It has been pointed out[2] that there is an inaccuracy in applying the laws of ideal gases to air-water vapor mixtures, since the presence of the air increases the water vapor pressure about 0.2 per cent, and further, the air absorbs an excessive amount of water vapor, giving an additional error of 0.3 per cent, or a total of about 0.5 per cent excess in the value for the relative humidity—an inaccuracy usually beyond the limits of observation. The principle of the wet-dry bulb hygrometer is the following: the dry bulb gives the air temperature, t_d. The wet bulb is surrounded by a wick saturated with water. The evaporation of the water from the wick absorbs latent heat from the wet bulb and lowers its temperature. There will always be a certain amount of sensible heat coming to the wet bulb from conduction and radiation, and the actual temperature will depend upon the balance between the latent heat lost and the sensible heat absorbed. The less the proportion of moisture in the air, the greater will be the evaporation and the lower the wet-bulb temperature, t_w.

The air is never at rest and the wet-bulb temperature will fluctuate with air currents. If, however, the air by means of a fan is forced past the wet bulb, the wet-bulb temperature becomes constant when the velocity is sufficient to remove the maximum water vapor evaporating from the wet bulb. With a proper wick an air velocity of 600 ft per minute at normal atmospheric pressures gives the minimum wet-bulb temperature. This air velocity can be secured either by moving the wet bulb through the air (*sling psychrometer*) or by moving the air past the wet bulb (*aspiration psychrometer*). To secure similar conditions for both wet and dry bulbs, both have always the same relative air motion.

The formula for the wet-dry bulb hygrometer is

$$p_a = p_w - AB(t_d - t_w)$$

where p_a is the actual vapor pressure, p_w the saturated vapor pressure at t_w, B is the ratio of the actual barometric pressure to the normal value, and A a factor depending upon the access of sensible heat by conduction and radiation. If p is in mm Hg, t in °C, with an air flow of 3 meters per second, and a suitable wick, A for mercury-in-glass thermometers and thermocouples is about 0.00057.[3] Access of heat to the wet bulb by conduction and radiation can be greatly reduced by diminishing the size of the temperature observing instrument. Less loss of latent heat by evaporation is required and consequently the air velocity by the wet bulb may be diminished. If thermocouples are used and the wet bulb junction is of No. 40 wire, copper-constantan or Nichrome-constantan, with a minute junction and a very light wick, the wet-bulb temperature, correct to within 0.5 °C, will be obtained in still air.[4] Consequently such *fine wire thermocouples* are *extensively used*, particularly in research laboratories and especially in small confined spaces.

The wick covering mercury bulbs and resistance coils is preferably of cotton, very thin, closely woven, fitting tightly and secured with the minimum of thread. In the case of very fine wire thermocouple wet bulbs, the wick consists of fine woolen or soft cotton yarn wound in a close single layer extending at least 1 cm on each side of the junction with the ends dipping into a reservoir of distilled water. The dry bulb should be above the wet bulb and distant at least 2 cm.

Many wet- and dry-bulb psychrometers are *made distant reading and recording*. With liquid thermometers the change of liquid volume is transmitted through a tube to a Bourdon gage, or a volatile liquid is used and the vapor pressure transmitted through tubing. Thermocouples and resistance thermometers are very simply connected by wires to the point of observation. To obtain a linear scale use is made of the approximate relations:

$$\frac{t_w - \text{constant}}{t_d - \text{constant}} \text{ is proportional to the relative humidity}$$

or

$$\frac{t_d - t_w}{t_d} \text{ is proportional to the relative dryness (100–R.H.}$$

For temperatures a little *below the freezing point of water* (0 °C, 32 °F) the wick may contain either liquid water or ice. Down to 27 °F or −3 °C, the calculated relative humidity will be the same within the limits of usual observational error, whether or not the wick is frozen, if tables with reference to saturation over undercooled water are used. The explanation is that the longer time required for equilibrium with ice usually results in sublimation of the ice from a portion of the wick and thus neutralizes the higher latent heat of sublimation of ice. Brooks has shown that an ice coating in place of a frozen wick gives satisfactory values if the value of the factor A is for ice rather than undercooled water.[5]

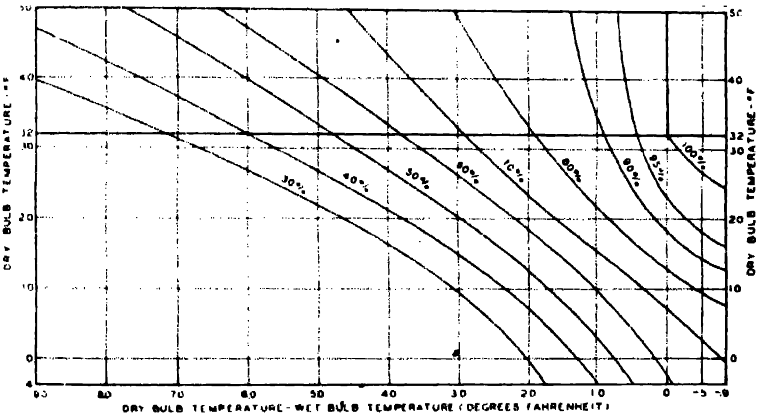

FIG. 1.

At still lower temperatures, measurement of the relative humidity is very difficult owing to evaporation of ice from the wick and the very low saturation vapor pressures. There is in addition *the ambiguity with reference to the definition of the relative humidity.*[6] Air will contain water vapor up to the saturation corresponding to undercooled water even down to at least −30 °C or −22 °F as shown by the careful observations of Prof. Ekholm and others in the Arctic regions. Consequently the air current passing over the wet bulb may deposit moisture if the relative humidity is high and the latent heat given up in the change from water vapor to ice may *raise the temperature of the wet bulb above that of the dry bulb.* German and English tables give the relative humidity with reference to saturation over undercooled water, the United States Weather Bureau tables with reference to ice. The portions of the American Tables covering low temperatures were not based upon experimental observations of the accuracy available today and give no data for wet-bulb temperatures above dry-bulb. The German Tables, which are with reference to undercooled water, recognize wet-bulb temperature above dry-bulb, but are founded upon limited experimental data. If both wet and dry bulbs read −18 °C, or −.4 °F, the humidity given in United States Weather Bureau Tables is 100 per cent, whereas in the German Tables the humidity is given as

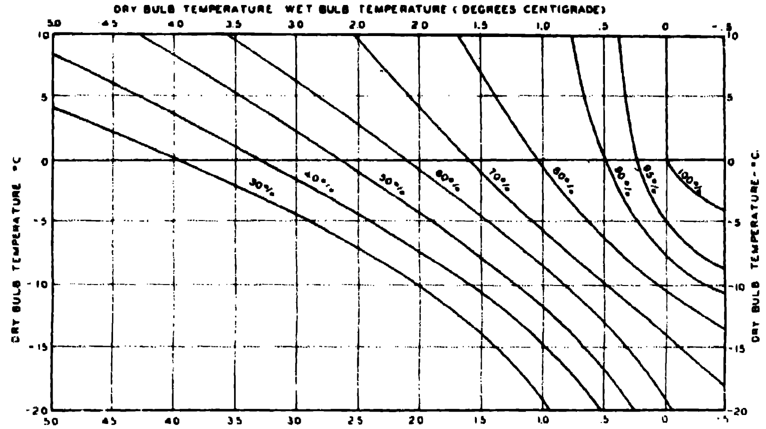

Fig. 2.

66 per cent and in the English Tables (see below) as 62 per cent. The most extensive and recent experimental study of psychrometric relations below the freezing point of water is that of Awbery and Griffiths,[7] based upon careful, simultaneous observations of dew point, dry bulb and aspirated wet bulb and finding the actual vapor pressure from the dew point. From the values for saturated vapor pressure of undercooled water at dew point and dry-bulb temperatures, obtained from the "International Critical Tables," the relation between dry-bulb temperature, wet-bulb depression and relative humidity was determined. Their results were presented in a table of relative humidities with reference to undercooled water for wet-bulb

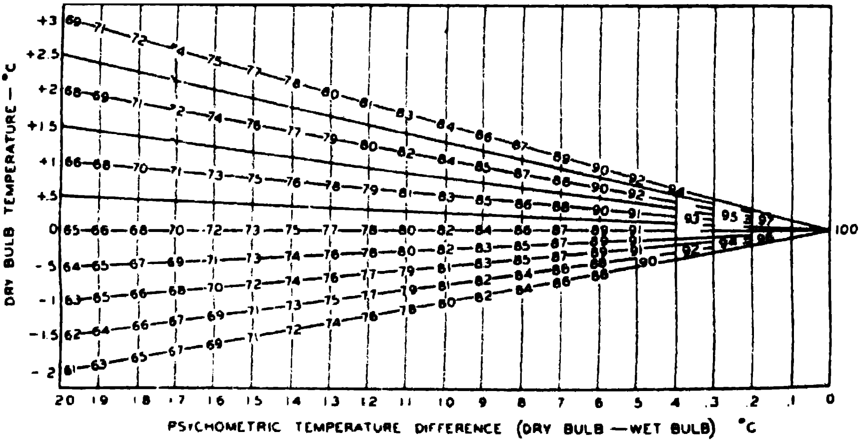

Fig. 3.

depressions from −0.1 to 4.2 °C and dry-bulb temperatures from 0 to −19 °C. This table was reproduced in the March 1938 number of *Refrigerating Engineering*. Curves of equal relative humidity convey a clearer picture of the relationships between dry-bulb temperature, wet-bulb depression and relative humidity than is obtained from a tabulation, and are much more convenient for practical use. From their table the writer has prepared two such charts, Fig. 1 for Fahrenheit temperatures, and Fig. 2 for centigrade temperatures. For comparison, the curves are extended above the freezing temperatures, psychrometric data given in modern tables being used. In view of the vast amount of such data for the region customarily considered in air-conditioning, the figure is limited to the region of cold-storage practice.

The writer has conducted humidity investigations in a great many low-temperature freezer rooms. The largest observed excess of the wet-bulb temperature over that of the dry-bulb was 0.3 °C, or 0.2 °C outside the table of Awbery and Griffiths. There are many freezer rooms today below −19 °C. However, the writer is unaware of any successful artificial humidification at freezer temperatures below the range of Figs. 1 and 2. The experimental freezer of Cook[8] gave 95 per cent relative humidity at 14 °F. Although not definitely stated, the humidity is apparently with reference to ice and, if so, is almost included in the charts which show that an aspirated wet-bulb thermometer in this freezer would have read about 0.6 °C or 1.0 °F above the dry-bulb thermometer. Figs. 1 and 2 suggest the difficulty, on account of deposition of moisture (wet-bulb temperature above dry-bulb), of obtaining humidities above the ranges covered.

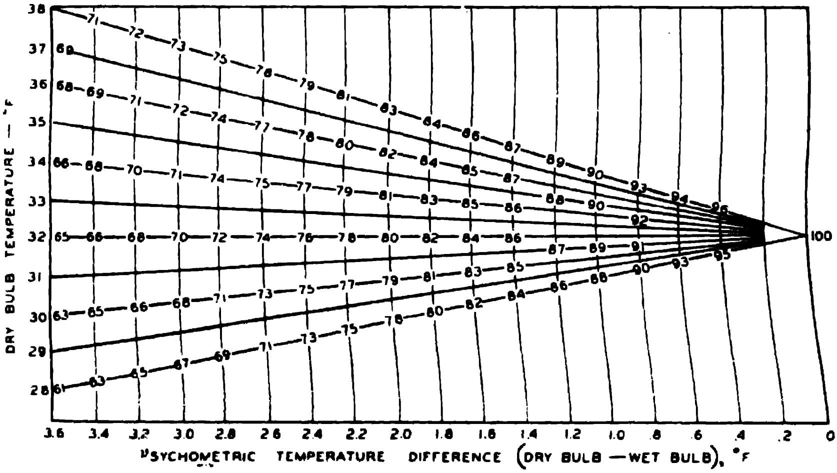

FIG. 4.

For a given dry-bulb temperature and psychrometric temperature difference the corresponding relative humidity with reference to ice can be found by multiplying the relative humidity with reference to undercooled water by the ratio of the saturated vapor pressure over the latter to that over ice. Values of this ratio are given by Johnson.[10]

Additional experimentation in low-temperature psychrometry is very much needed, extending to lower temperatures and higher humidities the work of Awbery and Griffiths, and corroborating their values for the humidities at low air temperatures and low psychrometric temperature differences which materially differ from those given in other tables. Unfortunately, the detail tables in their paper give neither observed dew-point temperatures nor state water phase, *i.e.*, whether ice or water.

Figs. 3 (°C) and 4 (°F) represent a method of psychrometric plotting introduced by the writer several years ago. It has proved so convenient for readily determining the relative humidity from the wet- and dry-bulb temperature readings given by sling and aspirated psychrometers that these two charts have been prepared for the temperature range of refrigerated cooler rooms.

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Electric Dew-point Recorder

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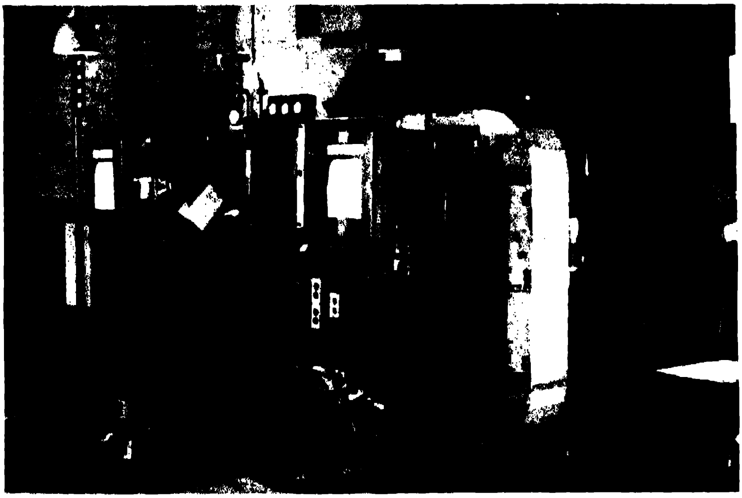
Humidity recording has increased in importance with the use of controlled air conditions in industry and other fields, improvements in industrial and agricultural drying machinery, and advances in the general field of research. This increased importance has encouraged the improvement of existing instruments and the development of new types.

Until recently most instruments for measuring humidity were either difficult to operate or limited in application. The latter is particularly true of the two common types of recording instruments used, the wet- and dry-bulb thermometer and the hair hygrometer. The ether-cooled silver thimbles used by Regnault,[1] Griffiths,[2] Holtzman,[3] and Stevenson and Babor [4] permitted very accurate observation, but were not adaptable to recording. Farbenind,[5] Tomlinson,[6] and Hixson and White [7] secured very accurate readings by using photoelectric cells to detect the formation of dew, but, as yet, have not developed their instruments as recorders.



Courtesy R. H. Reed, Univ. of Illinois.

FIG. 1. Constant-condition laboratory drier with which the electric dew-point recorder is used.

The electric dew-point recorder investigated by Johnstone [8] and Tchang [9] has many advantages over other instruments. Because of these, it has been used for several years in recording the dew point in a laboratory drier used in studying the rate of drying and the physiological response of hybrid seed corn, hay, and other agricultural products to the drying conditions.

The laboratory drier is shown in Fig. 1. It consists of a vertical duct in which the sample of material is suspended from a balance in a constant stream of conditioned air. The temperature is recorded, controlled, and maintained by the potentiometer at the left and a series of electric heaters totaling 21 kw. The instruments at the left of the right panel are part of the Thomas Meter for measuring the volume of air circulated in the drier. The potentiometer at the right records the dew point, which is maintained at the desired value by electric pencil-heater boilers that add superheated steam to the drying air. The power connections for these boilers are below the panel. The drier has been used a total of about four months this year, during which time dry-bulb temperatures of 90 to 161 °F and dew points of 58 to 114 °F were maintained.

The dew-point recorder consists of three elements: the metering unit, the vacuum-tube relay, and the recording potentiometer. These are shown in Figs. 2, 3, and 1.

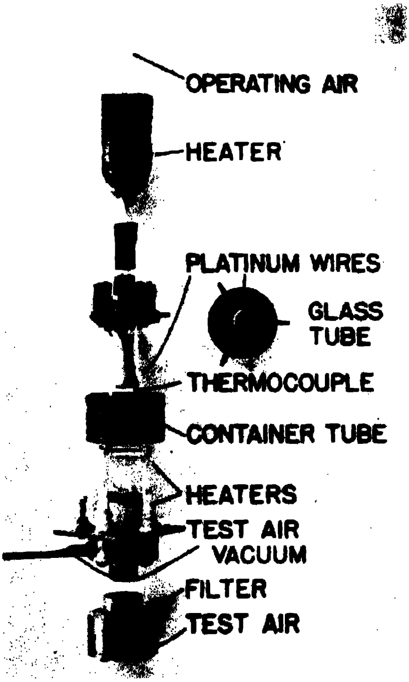


FIG. 2. The metering unit.

Metering Unit

The metering unit, Fig. 2, consists of a glass tube, a container tube, an air filter, and two heaters. The glass tube is a "Pyrex" test-tube with the closed end flattened. Two platinum wires, No. 24 B. & S. gage, are fused inside small glass tubes. These tubes are fused between the end of the test-tube and a thin glass plate. The wires are about one-sixteenth of an inch apart. Glyptal enamel is used to insulate the leads and to attach them to the tube. The surface of the glass plate is then ground to expose about one-third of each wire. An iron-constantan thermocouple, No. 28 B. & S. gage, is attached to the surface of the glass plate about one-eighth of an inch from one of the platinum wires, by means of a thin coating of glyptal enamel.

The container tube prevents mixing of the test air, the operating air, and the outside air. It also prevents stagnation of the test air and directs it so that condensation on the sides of the glass tube is prevented. The air filter removes dust particles from the test air as it enters the container. One of the two electric heaters is in the operating-air stream. The other heater is located on the outside of the container tube and is used to prevent condensation when the room temperature is appreciably below the dew point of the test air.

Vacuum Tube Relay

All parts of the vacuum-tube relay are shown in Fig. 3. The coil current at which the high-resistance relay closes is adjusted by varying the spring tension on the armature and the distance between the armature and the pole piece. During the past year these were adjusted until the relay closed with a current of 2.7 milliamperes.

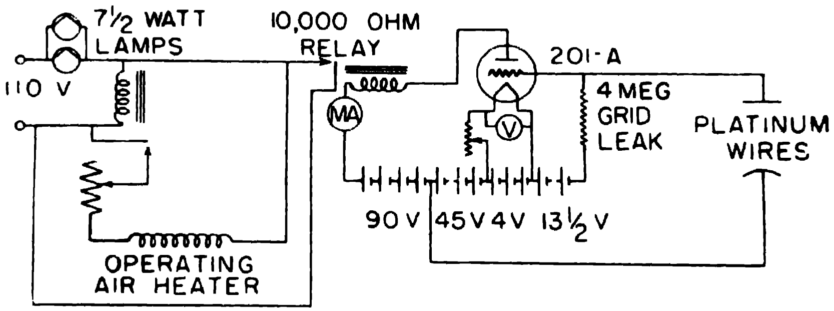


FIG. 3. Schematic diagram of a vacuum-tube relay.

Recording Potentiometer

The thermocouple fastened to the glass tube is connected to a conventional single-point indicating-recording curve-drawing potentiometer. The chart used has a range of 20 to 250 °F, a smallest division of 2 °F, and a nominal speed of 6 inches per hour.

The operation of the electric dew-point recorder is as follows: Operating air 10 to 20 °F colder than the dew point to be recorded is directed against the inside of the glass tube. This cools the outside surface of the tube until moisture in the test air surrounding the tube condenses on the ground glass surface between the platinum wires. This condensation causes the conductivity to increase gradually from less than 10^{-8} mho to as high as 4×10^{-6} mho for the unit as now constructed. Calibration of the instrument by chemical means has shown that the dew point corresponds to a conductivity of about 3.33×10^{-7} mho. The increase in conductivity changes the grid bias of the vacuum tube and permits current to flow through the coil of the high-resistance relay. This relay closes the low-resistance relay, which in turn connects the heater in the operating air stream. The heating of the operating air heats the glass tube and evaporates the dew. As soon as the conductivity is reduced the heater is disconnected. The lowest point in each cycle recorded by the potentiometer is the dew point.

The interest in instruments of this type varies. Therefore, the portion of this paper devoted to results will include items on its possible uses, the problems encountered in its development, and the general problem of its value as an instrument.

Accuracy

During the five years in which this apparatus has been used its accuracy and dependability have been increased by improvements in the metering unit, the vacuum-tube relay, and even in the potentiometer. In the last four months of use the calibration corrections were from 0 to 1 °F for most of the individual runs and exceeded 3 °F in only two cases, the maximum being 3.6 °F. The corrections were reproducible throughout a run unless equipment failure occurred, but changed with changes in the operating dry-bulb temperature and dew point, and following idle periods.

A study of the correction figures for different runs does not show a direct relationship between the corrections and the dry-bulb temperature and dew points. This indicates that the remaining inaccuracy is not a function of the operating conditions but is probably due to improper design or operation of the instrument. The following improvements are suggested: imbedding the thermocouple wires in, rather than on, the glass surface; the use of larger contacts and a more sensitive armature on the high-resistance relay to minimize changes in the closing current; the use of wire-wound rather than carbon-resistance grid leaks; and complete shielding of the metering unit from changes in temperature occasioned by changes in the dried operating and room temperatures.

Many of the investigators previously cited used hand-operated precision instruments to secure the accuracies of .1 to .01 °C which they report. These instruments can also be used with the present apparatus to secure greater accuracy. However, when a record is desired, some accuracy is sacrificed. Thus, it is likely that even with the improvements previously mentioned, the overall accuracy of the recorder, without calibration correction, will not be higher than, and may be less than, the inherent accuracy of the recording potentiometer. With the 20 to 250 °F range used, the accuracy of adjustment of the potentiometer is .7 °F.

Sensitivity

The electric dew-point recorder will consistently record the change produced by 0.05 ampere variation in the current flowing through one of the electric steam boilers when that change raises or lowers the dew point only about .2 °F.

Frequency of Recording

Each metering unit has an inherent cycle frequency which can be varied only within certain limits. When the temperature of the cooling air is reduced, the frequency increases until it may reach a cycle time as short as 10 seconds. However, periods of less than about 75 seconds are unsatisfactory because the potentiometer is unable to follow the rapidly changing temperature, and the glass tube cools below the dew point before the operating-air heater has become effective. Reducing the temperature differential to prolong the cycle is effective until drops of water condense on the sides of the glass tube before dew is formed on the ground surface. Changing the voltage on the operating-air heater has very little effect. Reducing the voltage prolongs the heating period, whereas increasing it shortens the period, so that approximately the same heat is produced at all settings. A delayed relay would prolong the heating period and reduce the frequency.

Alternating-current Vacuum-tube Relay

A vacuum-tube relay with rectifier and filter has been successfully operated from an alternating-current supply. The direct-current unit is being used, however, because equipment has not been available to compensate for a 13 per cent fluctuation in the alternating-current supply line voltage.

Acknowledgment

The assistance of Dr. H. F. Johnstone, Professor of Chemical Engineering, and Mr. F. R. Wiley, Technician in Agricultural Engineering, in solving the numerous problems encountered in developing the electric dew-point recorder is gratefully asknowledged.

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The Construction and Use of a Thermoelectric Psychrometer

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Many problems involving the study of gases are concerned with the measurements of their moisture contents. Determination of the humidity of the air is made difficult in many cases where the usual methods cannot be employed. Limited space, measurements at remote points, or conditions of little or no air movement eliminate use of the sling psychrometer. The sampling method of the Assmann is not permissible where it is necessary to maintain still air conditions. Small-scale hair hygrometers may be used to advantage in some instances, but these instruments are subject to unfavorable variations in calibration.

These problems have led to the investigation and development of the thermoelectric psychrometer, one type of which it is the object of this paper to describe.

The instrument of the general type described here was originated in Germany by Wald,[1] Cammerer,[2] and Koch.[3] Work of the same nature also was done in England by Powell.[4] The development of the instrument by Cammerer was based on the heat-transfer principles governing free convection from horizontal cylinders. A plot of the dimensionless criteria of Nussult's Modulus as ordinate against the product of Grashof's and Prandtl's Numbers as abscissa shows this curve to be horizontal for small values of Gr.×Pr. Thus in the region of values representing cylinders of small diameters, Nu. is a constant, and the film conductance per unit area varies inversely as the diameter. Referring to the analogy between heat transfer and diffusion, the mass-transfer film conductance is shown to vary inversely as the diameter for free diffusion from small horizontal cylinders. This is the basis for the operation of the thermoelectric psychrometer employing wires of small diameter.

The instrument as made by Cammerer consisted of a set of three wet and three dry thermocouples connected in series, the wet junctions being moistened by means of cotton wicks and an eye dropper. The chief disadvantage, which led to the particular design described here, was the short time available for measurement with the instrument between successive wettings of the wick. This period was about fifteen minutes over the average range of relative humidity, and in the measurement of humidity gradients over traverses of several hundred feet above the earth's surface, was far from sufficient. The need for a means of keeping the wick wet over a comparatively long period of time, as well as the desirability of a smaller instrument, resulted in the development work which led to the present design.

Because of the widespread applications possible with the thermoelectric psychrometer, it is thought desirable to describe completely the several steps in the construction of the instrument as used by the author.

The thermocouple supports, the water reservoir and the system for the distribution of the water to the wicks are incorporated in one unit, as shown in Fig. 1. This unit consists of a glass spider with six tubular arms extending radially from the central reservoir. A larger vertical tube employed for filling the reservoir also provides a means for mounting the instrument. The end of each radial tube is turned upward, as shown, and drawn to a small diameter in order to decrease the opening. This tends to hold the wick firmly, and the surface tension of the water brings the liquid to the top of the tube. Each tube or arm is provided with an eye through which the thermocouple wire is threaded. One of the arms has two eyes to allow for the fastening of the wire leads.

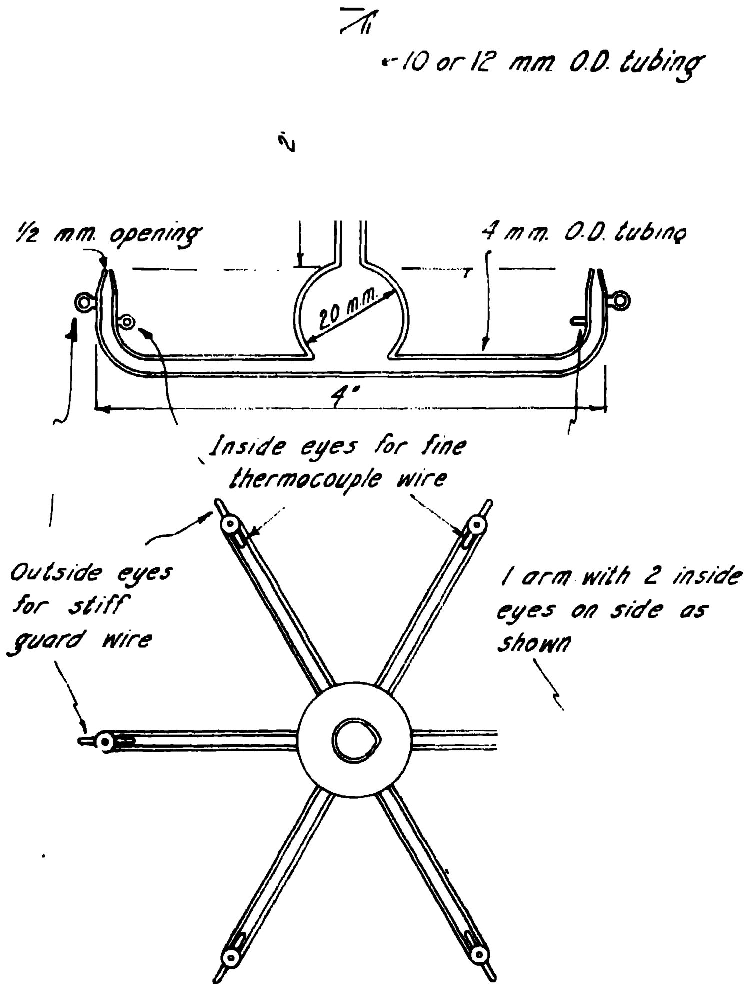
10 or 12 mm O.D. tubing
½ mm opening
4 mm O.D. tubing
20 mm
4"
Inside eyes for fine thermocouple wire
Outside eyes for stiff guard wire
1 arm with 2 inside eyes on side as shown

Fig. 1. Thermoelectric psychrometer.

This arrangement provides for six thermocouple junctions in series, each alternate junction being covered by a wick. Copper-constantan couples were used on the instrument, so that the completed thermocouple series contained a copper lead at each end. These were joined to two copper wires of larger gage to facilitate handling and connecting to the potentiometer for measurement. With this construction, the instrument then measures three times the wet-bulb depression. An additional thermocouple is employed to measure the dry-air temperature.

With the glass spider constructed, two steps remain in the completion of the psychrometer. These are the forming of the thermocouple series and the covering of three of the junctions with wicks. One of the most important requirements of the instrument is that the overall diameter of the wire and wetting wick does not exceed 1 mm or 0.04 inch. Since this is essential to satisfactory operation, butt-welded thermocouple junctions are necessary. Several methods were tried in building the couple joints. It was found that fusion of the copper and constantan by means of an electric current resulted in embrittlement of the wires near the weld with a loss of resistance to bending and handling. Silver-soldered butt joints proved very satisfactory, and were finally used on all the psychrometers made by the author. This method entails some difficulty when working with wires of size 36 or 40, but experience soon makes possible the production of neat and efficient junctions. The procedure is as follows.

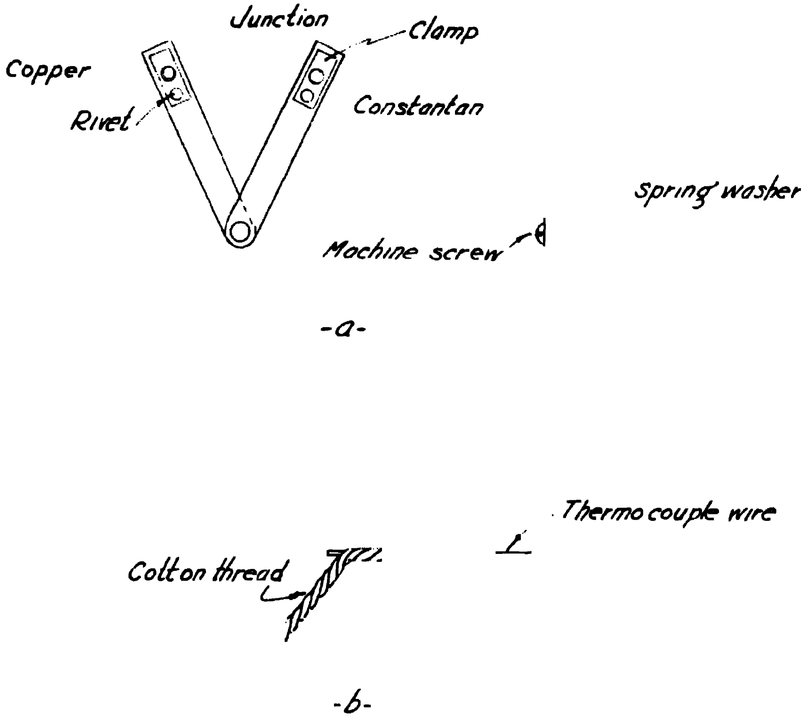

FIG. 2. Thermoelectric psychrometer.

Copper and constantan wires of either of the above sizes are cleaned carefully and cut to approximately the correct lengths. The tips of the wires are then cut with a small, sharp scissors, giving clean, square ends. A small gas flame, not over three-sixteenths of an inch high, is used in the soldering process. A wire is wetted at its tip and dipped in finely powdered borax as flux, and held over the flame to form a small, clear bead which completely covers the wire's end. This is important, since it is essential that the silver solder form a thin layer at the tip. When the bead has been made, the tip is again wetted and dipped in silver solder filings, then heated to a dull red, or to a temperature just sufficient to melt the solder.

Care must be exercised in heating so that the wire does not come too near or enter the flame, since this results in oxidation of both wire and solder, and the process must be repeated.

After tinning all the wire tips, a copper and a constantan length are mounted in the small, adjustable frame as illustrated at (a) in Fig. 2. This frame is simply two small metal arms pinned at a common movable joint provided with enough friction to maintain any position, and with clamps at the outer ends for holding the wires to be joined. This allows the ends of the wires to be brought together and perfectly aligned. Heating again to a dull red now fuses the solder and results in the desired butt joint. This procedure is repeated until the complete set of junctions is made. The junctions may be tested for strength by rolling them between two flat surfaces. This operation also tends to produce a small, smooth regular joining.

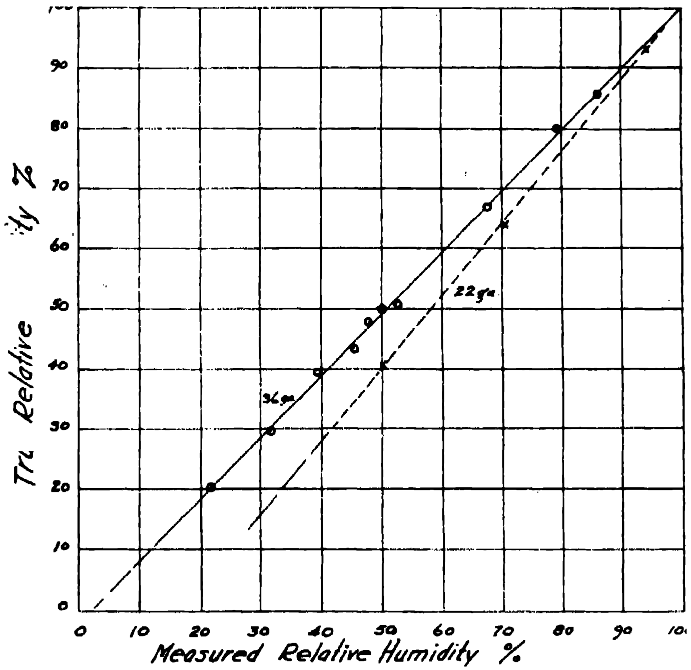

FIG. 3. Calibration-thermoelectric psychrometer. 36-gage and 22-gage copper-constantan thermocouples. Still air conditions.

Perhaps the most difficult operation is that of placing the wick on the wet junction. Since it is important that the diameter of the wire and wick together does not exceed 0.04 inch, care must be exercised both in the selection and application of a suitable wetting material. The author has used thread made with absorbent cotton, dental floss from which the dressing was removed by boiling in water, cotton thread subjected to the same conditioning, and strands of cotton fabric. The last material proved most successful, since the fibers were relatively short and yet the thread or strand retained sufficient strength to permit ordinary handling. The most satisfactory method of applying this wick has been to unravel the threads slightly, which separates the fibers, and threading the wire axially along *the center. By advancing the wire a fraction of an inch at a time, as shown at (b) in Fig. 2, through the side of the wick, the thread may then be untwisted and the fibers rewound around the wire. The wick must cover at least three-quarters of an inch of wire.*

The butt-welded junctions of the thermocouple series permit the wicks to be moved to their proper positions, and the large eyes of the spider allow threading of the whole thermocouple and wick assembly in the supports. When the wires are set so that the junctions are midway between the eye supports of the several arms, the cotton thread ends are placed in the openings of alternate arms, and the instrument assumes the completed form shown in the photograph.

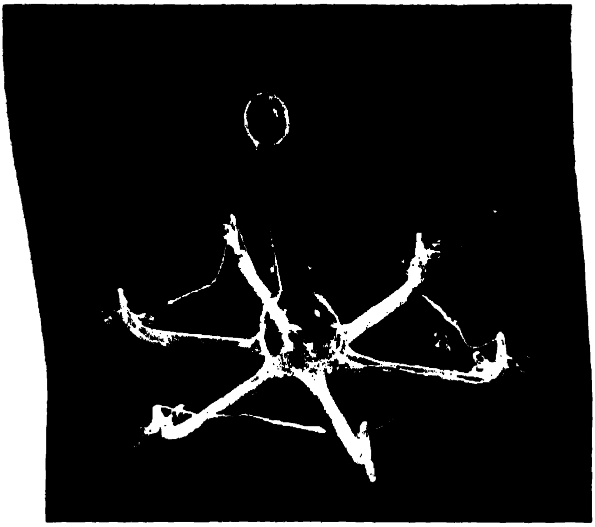

FIG. 4. Photograph of completed instrument.

Calibration is necessary in order to render the instrument useful. Fig. 3 shows a calibration curve for this type of psychrometer. The solid line represents the calibration of an instrument employing 36-gage copper-constantan thermocouples. It will be noted that the ratio of the measured relative humidity to the true value is larger for lower humidities. This may be due to any of several variables, such as conduction of heat along the wire, very small spaces in the wetting wick near the junction, or tightly wound portions of the wick causing the water to travel along the outside of the wetting material. These sources of error, although small, are variables entering each separate instrument in different combination. It must be remembered, therefore, that the calibration curve shown is merely an indication, and that each instrument should be calibrated over the range through which it is to be employed.

Although results of all tests made on the thermoelectric type of psychrometer are not shown here, the effect of using wire of larger gage is indicated by the dotted line, Fig. 3. This curve represents the calibration of an instrument using 22-gage copper-constantan wires and with wet junctions covered by cotton thread. In this case the conduction of heat along the wire was enough to give only a fraction of the true depression of the wet-bulb temperature.

It has been shown in other investigations that a cold air pattern is formed around the wet junction of the instrument due to evaporation of the water from the wetted wick. The influence of this pattern, due to the falling of the heavier, cooler air, extends some distance below the wire. It is necessary, therefore, in measuring relative humidities, to place the thermocouple for the determination of the dry air temperature to the side of or above the wet junctions.

Several uses of the instrument in the form described here have been made, and satisfactory results obtained. Besides the use for measurement of the humidity gradients in and above citrus orchards, the instrument has found application in dehydrators and in the measurement of the moisture content of the air in sugar-beet storage piles.

It has not been the primary object of this paper to discuss the theoretical bases for the functioning of the thermoelectric psychrometer, but rather to present sufficient data to allow the investigator to construct an efficient instrument for the measurement of humidity. Nor is it necessary that the exact design presented here be closely followed. H. S. Gordon, University of California, Davis, Cal., has constructed and used a single junction each for the wet and dry thermocouples, with the junctions formed by plating copper on constantan wire. The plated couples make a very satisfactory instrument, although the thermoelectric response is somewhat reduced. In cases where the wet-bulb depression is relatively large, the single wet and dry junction instrument provides sufficient accuracy.

These examples of design and use of this type of instrument not only illustrate its many applications, but indicate the distinct advantage over other means of measurement of relative humidity in that a particular design may be made to fit a specific function.

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Characteristics of Thermocouple Anemometers

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The problem of measuring the velocity of convection currents of air arising from temperature differences of a few degrees is encountered in studies of processes involving heat transfer by convection. For example, in an iced refrigerator car filled with warm fruit, the effectiveness of the ice in cooling the load is almost entirely dependent upon convection. Conduction and radiation are of only minor importance. The rate of movement of air is a principal controlling factor in refrigerator cars, refrigerated storages and in convection-heated spaces of all kinds. Ordinary methods of measuring air flow are of little service for velocities of fractions of a foot per second or in air passages which are difficult or impossible to enter when readings are desired.

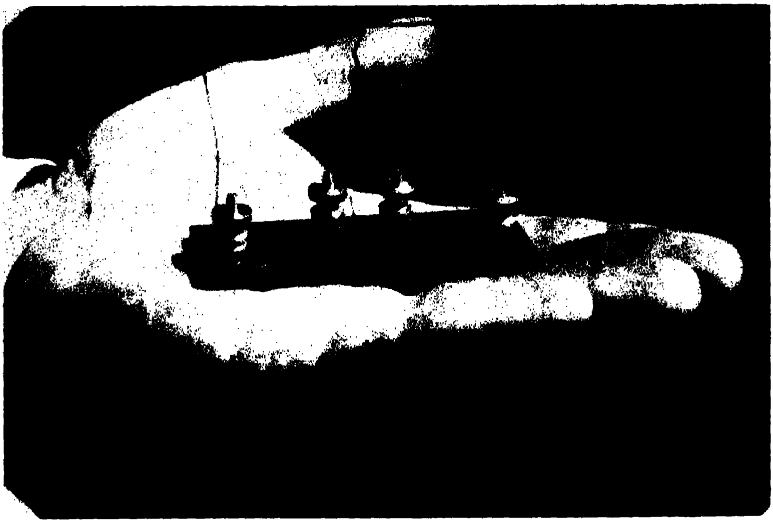

FIG. 1. Thermocouple anemometer.

For the particular purpose of measuring air velocities under the floor racks of loaded refrigerator cars, an anemometer has been developed and found useful in many applications where other instruments cannot be used with complete satisfaction. It consists essentially of a thermocouple, both junctions of which are exposed to the air stream and one junction of which is heated. The difference in temperature between the junctions depends on the cooling effect of the moving air, and by suitable calibration, readings of the electromotive force of the thermocouple may be translated to air velocity.

Fig. 1 shows the anemometer mounted on a hard-rubber base with binding posts for connecting the leads. The thermocouple is of No. 24 B. & S. gage copper and constantan wires. The constantan is but one inch long and is butt-jointed to the copper with silver solder, making two junctions one inch apart. One of the junctions is wrapped with about 60 turns of No. 40 Nichrome wire, through which an electric current of known amperage may be passed. Normally a current of about .05 ampere is used. In still air this current raises the temperature of the heated junction to about 50 °F above that of the cold junction and an electromotive force of one millivolt is set up in the thermocouple.

With this instrument velocities as low as six feet per minute may be measured. This lower limit may be reduced to between two and three feet per minute by modification of the construction. The anemometer may be set in position for reading, and with the lead wires extending as far as is desired, readings may be taken without the presence of an observer to disturb the air currents. For example, air velocities under the floor rack of a loaded refrigerator car are read with a potentiometer on the roof of the car so that it is not necessary to open the car doors or otherwise disturb conditions inside. Lead wires 50 to 100 feet long are commonly used to connect the anemometer to the potentiometer, since the length does not affect the precision of the reading.

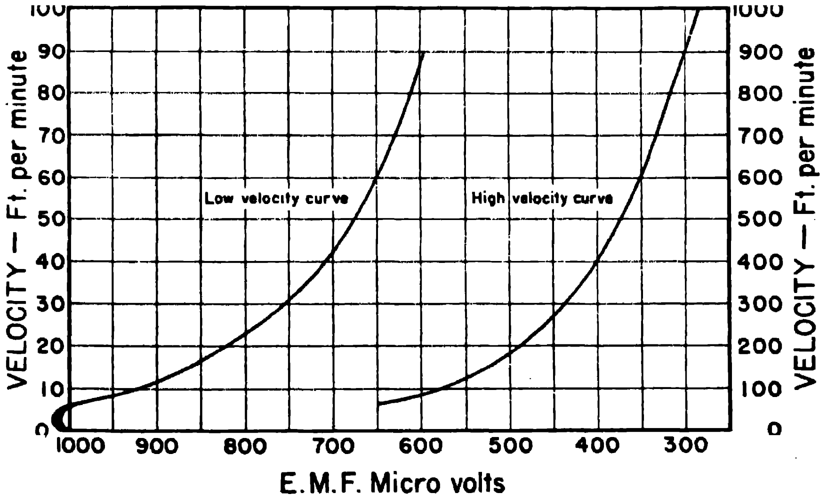

FIG. 2. Relation between velocity and electromotive force for thermocouple anemometer.

The anemometer is calibrated by moving it at known velocities on a whirling arm in still air. A typical calibration curve is shown in Fig. 2. It is found that the same relation between air velocity and thermocouple electromotive force exists for all individual instruments made in the same way, so that a common conversion chart can be used for all. On the other hand, the amount of heating current required for establishing the emf velocity relation shown in Fig. 2 may not be the same for different individuals of apparently similar construction. This makes it necessary to determine by test the amount of heating current required by each anemometer. It will be noted that the curve in Fig. 2 passes through 60 feet per minute at 650 microvolts. This has been chosen arbitrarily as the reference point. That is, when a new anemometer is to be put into use, it is rotated in the calibrating chamber at a linear speed of 60 feet per minute. The current through the heating coil is adjusted until a reading of 650 microvolts is secured on the thermocouple terminals. This current is measured and the same amperage is used in all subsequent measurements of air velocity with that anemometer.

This type of anemometer has been in use for several years, and it is now possible to point out some of the characteristics which seem to be inherent in the instrument. Since one junction is at a temperature above that of the air, it heats the air in contact with it and sets up a convection current. This is, of course, characteristic of any anemometer which uses cooling effect as a measure of air velocity. For this reason, a vertical air current does not have the same cooling effect as a horizontal current of equal velocity. Nor do upward and downward vertical currents have equal cooling effects. The calibration curve for horizontal velocities (Fig. 2) therefore is only approximately correct for air currents moving upward or downward. The convection current set up by the heated junction appears to have a greater effect at low velocities (below 8 or 10 fpm) than at higher velocities. It has been observed that when the velocity is below about 6 or 8 fpm, the thermocouple reading continually drifts over a small range even when the air stream is steady. The amplitude of the drift increases as the air velocity becomes lower. This is illustrated in Fig. 2 by the broadening of the line at low velocities. It will be noticed in Fig. 2 that as the air velocity decreases, the emf of the thermocouple increases until a velocity of about 2 or 3 feet per minute is reached, when further decrease in velocity results in a decrease in emf. This shows that, at extremely low velocities, increased general air movement tends to raise the temperature of the hot junction rather than to lower it. Since this is contrary to the effect which might be expected and which does obtain at higher velocities, the following possible explanation of the cooling effect at extremely low velocities is offered, although no experiments have been set up to prove its validity.

Suppose the anemometer is exposed to air which is not moving. When the heating current is turned on, the temperature of the heated junction will rise and a small convection current will be set up, air in contact with the wire rising vertically in a smooth stream. This stream of air, being unbroken for an appreciable distance, will constitute a virtual chimney and will draw air past the heated wire in accordance with the height of the chimney effect. This air drawn past the wire will tend to cool it. Now, if a very slight horizontal movement of air takes place, the rising stream of air will be disturbed and broken into a less regular stream and displaced to one side. Accordingly, the chimney effect will be lessened, and less air will be drawn past the wire by convection. The net movement of air past the wire will be the vector sum of the horizontal movement and the vertical convection movement. Slight horizontal movement apparently reduces the vertical movement to such a degree that the net velocity past the wire is lower than if there were no horizontal movement. The minimum net velocity occurs when the horizontal velocity is about 2 or 3 feet per minute. At about 6 feet per minute (of horizontal movement) the horizontal component has increased enough that the net movement past the wire is about the same as with no horizontal movement. At higher velocities the convection becomes less effective, although it may account for the drifting of the thermocouple reading at velocities somewhat higher than 6 fpm.

The characteristic reversal of the cooling effect described above sets a minimum velocity, below which unique readings of velocity cannot be made. That is, the calibration curve shown extends to zero feet per minute, but cannot be used for velocity measurements below 6 fpm. The reading at 4 fpm, for example, is about the same as at 1 fpm.

If it is desired to read velocities lower than 6 fpm it is found that the minimum readable velocity can be lowered by reducing the heating current. For example, by using only one half the heating current, the resulting calibration permits reading velocities down to about 4 fpm. This, however, is at the expense of reducing the temperature difference between the junctions to about one-fourth of its original value, and therefore reducing the accuracy with which readings can be made.

The size of the wires affects the lower limit of readable velocities. By using No. 35 wire instead of No. 24 for the thermocouple, and wire .0015" in diameter instead of .0031" in the heating coil, the limit is reduced to about 3 fpm without any sacrifice in accuracy. This small type is difficult to construct and is very fragile. By using this small type and reducing the heating current so that the temperature difference between the hot and cold junctions is of the order of .3 millivolt, a usable calibration down to 2.2 fpm has been obtained.

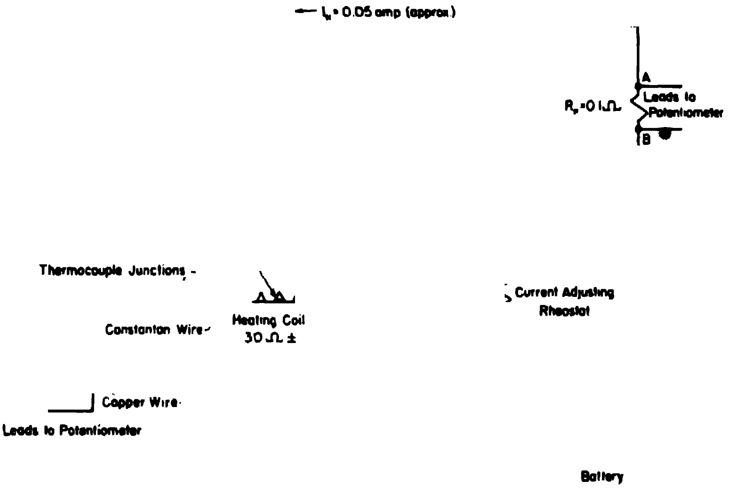

FIG. 3. Simple thermocouple anemometer circuit.

Any two metals having different thermoelectric powers can be used in the thermocouple. Copper and constantan are readily available in the proper size. Manganin was substituted for the copper in some. The thermoelectric power of manganin is about equal to that of copper, but its thermal conductivity is lower. When manganin is used, less heat is carried away along the wire and less heating current is required to maintain a given temperature difference between the junctions.

The cold junction of the thermocouple anemometer is immersed in the air stream to be measured. It, therefore, assumes a temperature approximately equal to that of the air. The thermocouple furnishes a measure of the rise in temperature of the heated junction due to the heating current. Since the emf per degree of a copper-constantan thermocouple changes slightly with changes in mean temperature, it is to be expected that when the temperature of the air stream changes, the characteristic relation between air velocity and thermocouple emf for a given heating current will be changed. It has been observed that such a change takes place. That is, if an anemometer has been calibrated in air at 80 °F, that calibration will be only approximately correct at other temperatures. For many purposes the discrepancy may be neglected, but it should be recognized that there is a temperature correction. This difference in reading can be compensated by changing the amount of heating current. With an anemometer of the type whose calibration-curve is shown in Fig. 2, it has been found that to give the emf velocity relation illustrated in the figure, the heating current needs to be about 2 per cent greater at 30 °F than at 80 °F air temperature. By measuring the temperature of the air stream the proper adjustment of heating current may be made for reading the velocity. This correction, when demanded by a requirement for accuracy in readings, makes the operation of the instrument less simple. To avoid the necessity for reading the temperature and readjusting the heating current accordingly, a circuit for making this correction automatically has been devised. The circuit for the simple anemometer is shown diagrammatically in Fig. 3, and that for the temperature compensated and standard current types in Fig. 4.

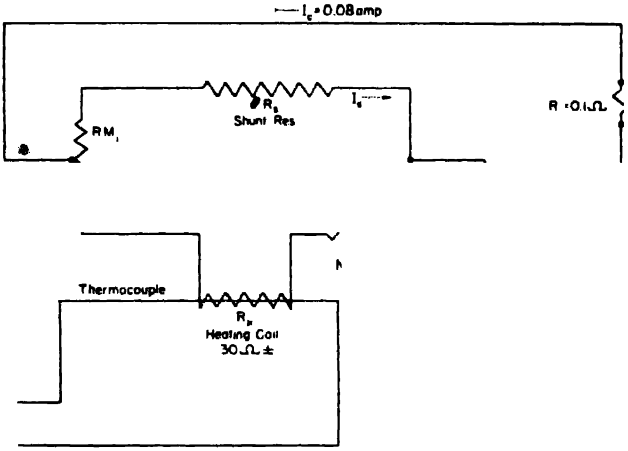

FIG. 4. Thermocouple anemometer heating circuit for temperature compensation and standard current.

In Fig. 3 the heating circuit is shown to consist of the heating coil which is wrapped on one junction of the thermocouple but not in electric contact with it, the battery, the standard resistor (across which the potential drop may be determined and used as a measure of the current flowing in the circuit) and the current-adjusting rheostat. In using the instrument, the heating circuit is closed and an observation of the potential drop across the standard resistor is made with a potentiometer. The rheostat is adjusted until further observation of the potential drop indicates that the predetermined amount of current is flowing in the circuit. A reading of the electromotive force between the terminals of the thermocouple is then made, and by reference to a curve such as that in Fig. 2, the air velocity measurement is completed.

The circuit shown in Fig. 4 is similar to that in Fig. 3 and readings are made in the same way. However, a shunt has been placed across the heating coil of such resistance that when a current of I_c which has the same value for all anemometers, is passed through the standard resistor AB, the current, I_H, going through the heating coil is of the proper amperage for that particular anemometer. In addition, a temperature-sensitive resistor, R_N, is placed in series with the heater coil so that if the temperature of the air stream is high, I_H will be reduced, or if low, the current will be increased, in accordance with the changing current requirements at different ambient temperatures.

It has been found that with a copper-constantan thermocouple, size 24 B. & S.

gage, the current should be increased by one part in 2500 for each degree Fahrenheit drop in temperature in the range 30 to 80 °F, the following equations showing the relations between the resistances and currents involved:

Referring to Fig. 4, let R_s and R_{M1} be grouped together as R_1, and R_N, R_H, and R_{M2} be grouped as R_2 so that

$$R_1 = R_s + R_{M1}$$

and

$$R_2 = R_N + R_H + R_{M2}$$

then

$$I_H R_2 = I_S R_1 = (I_c - I_H) R_1$$

$$I_H = \frac{(I_c - I_H) R_1}{R_2}$$

$$I_H = \frac{I_c R_1}{R_2} - \frac{I_H R_1}{R_2}$$

$$I_H + \frac{I_H R_1}{R_2} = \frac{I_c R_1}{R_2}$$

$$I_H \left(1 + \frac{R_1}{R_2} \right) = \frac{I_c R_1}{R_2}$$

$$I_H = I_c \frac{R_1}{R_1 + R_2}$$

I_c may be considered constant since it is always brought to a standard value before a reading is taken. R_1 is the sum of R_s and R_{M1} and is constant once the location of point M is established for the anemometer. The heating current then is inversely proportional to the sum of all the resistances included in R_1 and R_2. From calibration at different temperatures, it is desired that the heating current increase one part in 2500 for each degree drop in the temperature of the air stream. If the amount of nickel wire (or other wire having a sufficient temperature coefficient of resistance) in R_N is so adjusted that the decrease in resistance of R_N for each degree drop in temperature is $\frac{1}{2500}$ part of the total, $R_1 + R_2$, the heating current will automatically increase by the same proportion. Since the range over which the anemometer is normally used is not over about 70 °F (from 30 to 100°) this reciprocal relationship gives adequate accuracy of temperature compensation.

In order to permit the use of a standard current I_c, the same for all anemometers, even though the heating current I_H may vary with different anemometers, the proper relation between I_c and I_H is obtained by adjusting the location of the contact M. This is done by trial while the instrument is moving in still air at known speed.

The circuit shown in Fig. 4 provides two modifications in operation. The temperature-sensitive resistance automatically applies a compensation for error due to the air stream temperature; the shunt permits initial adjustment of each instrument so that even though different individuals require different heating current, the current supplied to the circuit may be made the same for all.

A number of characteristics of the thermocouple anemometer have not been investigated. No extensive tests have been made on the effects of air composition for example, although calibrations made at high and low humidities indicate that moisture content of the air is of minor importance. Large percentages of carbon dioxide would no doubt affect the relation between air velocity and thermocouple reading, although no tests of this effect have been made.

The nature of the air motion, whether stream-line or turbulent, may also affect the anemometer reading.

All the foregoing comments are based on experience in field and laboratory use and on calibration by one method only. This was by rotation at known velocities in still air in a tight box in which the possibility of convection currents was reduced to a minimum. Calibrating was done before the instrument was mounted for use. The question arose whether calibration by some other method would give different results. The calibration of one anemometer was tested in a tube in which the velocities were measured by a Thomas meter. At low velocities the agreement between the original calibration and the Thomas meter corrected reading was not good. The anemometer calibration showed 9 fpm in an air stream in which the Thomas meter showed 12.5 fpm. At higher velocities the percentage difference between the readings was less. The reason for this discrepancy has not been determined, but it is hoped that further calibration by other means will render the anemometer readings as accurate on an absolute basis as they appear to be on a relative basis. In spite of the lack of an absolute standard for checking the calibration of these instruments, they have proved useful in studies of air currents in refrigerator cars, storage houses, grain bins, and farmhouses in which heating tests are made, and in many cases have furnished data which was not obtainable with any other available instrument.

Discussion

G. B. Schubauer, National Bureau of Standards: Mr. Hukill has not pointed out that other heat-loss anemometers have been used to measure air speed, such as the hot-wire anemometer and several varieties of heated liquid-in-glass thermometers. The hot-wire anemometer is the most widely used instrument of this kind, and differs from the thermocouple anemometer mainly in that the rate of heat loss from the hot-wire, which depends on the air speed, is determined by the change in resistance of the wire when carrying a constant current or by the current required to maintain the wire at a given temperature difference. At very low speeds, comparable with the convection current rising from the heated wire, the hot-wire anemometer shows an anomalous behavior like that shown in Fig. 2 for the thermocouple instrument.

It is suggested that the thermocouple instrument, like the hot-wire anemometer, might be operated at a constant temperature, using the change in heating current to indicate the speed, and might thereby suffer less reduction in sensitivity as the speed increases. It appears that the performance at very low speeds could be improved by this method of operation.

A comparison of the relative merits of the two instruments on the basis of the information at hand fails to show any real advantage of the thermocouple anemometer over the hot-wire anemometer. Apparently one advantage possessed by the hot-wire anemometer is that the voltage drop across the hot-wire element generally used is several volts, and changes in this voltage drop with speed are of the order of millivolts rather than microvolts, as is the case for the thermocouple anemometer. On the other hand, a heated thermocouple appears to be inherently more rugged than a hot-wire and may be less likely to change calibration.

Assuming that King's equation for heat loss applies to the thermocouple anemometer as well as to the hot-wire type, it appears that changes in the thermal conductivity of the air with changes in ambient temperature must be taken into account, together with changes in the thermoelectric power of the couple. It is noted that these two effects are in opposite directions for the couple used, and therefore partially compensate each another. A similar compensating effect exists between the resistance of a hot-wire and thermal conductivity. In neither case, however, is the compensation complete, and the residual effect must either be taken into account or be eliminated by an auxiliary compensating device.

Control and Measurement of Temperature Under the Microscope

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For more than a hundred years men have been constructing apparatus to control the temperature of microscopical preparations. They have used these devices to observe changes in structure during the hardening and annealing of steel, to watch transformations in rocks at the temperature of molten lava, to determine the crystal systems of frozen gases of the atmosphere, and even to study the influence of temperature on the supposedly spontaneous generation of life. A system of micro-identification of organic compounds has been largely based upon the determination of melting points by means of a microscope hot-stage.

In the literature which has arisen from these researches, many extremely valuable instruments are described. Some important objectives have been attained, but there has not been a definite trend toward improved apparatus. New types do not seem to be based upon a knowledge of old ones, and a device described or marketed this year may be neither simpler nor better than another that is seventy-five years old. Partly because of inadequate descriptions and partly because there have been few impartial comparisons of indicated temperatures with the temperatures at which known phenomena occur, no clear picture has emerged of the relative merits of these different contrivances.

Difficulties of Accurately Measuring Temperature with Hot-Stage Apparatus

The problems of attaining and controlling temperature in high-temperature microscopy are much simpler than has often been imagined. Practically any of the devices listed in the voluminous literature[1] will work satisfactorily within its suggested range. It is only when temperature measurements must be accurate within one or two per cent of the departure from room temperature that troubles are encountered. Very brief reading makes it plain that each completed device needs calibration even apart from the calibration of its thermometer. A few quotations will make this plain. M. P. Cram[2] wrote of an apparatus which he had described, "The temperature of the thermometer of course is not that of the substance on the slide, but by noting the temperature at which an unknown substance melts the true melting point can be found by comparison with substances of known melting point." B. A. Rogers[3] described one of the best instruments for observing changes in metals, but wrote, "Using 960.5 °C as the melting point of silver, it was determined that readings were about 1.6 per cent too low." Although Klein[4] reported the errors in his apparatus to be negligible, Kofler and Hilbck[5] found these errors to be 5 to 8 °C at 150 °C, while Linser[6] found them to be greatly dependent on the rate of heating and thickness of glass slide and to be about 11.5 °C at 290 °C.

There are conditions, vital for accurate measurements of temperature, which are so easily attained in ordinary macro-experiments that their importance tends to be forgotten. The material being studied and the measuring element should both be surrounded by a medium relatively large in extent and of relatively large heat capacity. The temperature of part of this medium must be the same as that of the material being studied. To assure this uniformity it is necessary that the conditions for heat transfer within the region be relatively favorable. Moreover, the opaque surfaces of the entire solid angle surrounding the region of measurement should be at about the same temperature. A departure from any of these conditions influences the measured temperature. In most types of experiment the volume, uniformity of temperature, heat capacity, and conductivity of the matter immediately surrounding the point of measurement are so great that their effects predominate. Usually other effects, such as those of stem emergence, conduction of heat along thermocouple or resistance-thermometer leads, and radiation to and from opaque objects are so small that satisfactory corrections are easy. In general, the effects of the observing and temperature-measuring instruments upon the temperature itself are insignificant.

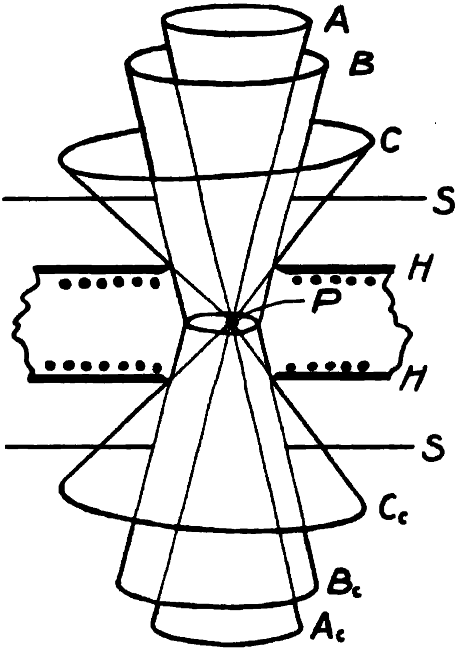

FIG. 1. Limiting angles through which light must pass and heat escape in a microscope hot-stage.

P is any point within the circular field (represented as an ellipse). H and H are parts of the heating element. S and S are shields which protect lens parts from radiation. A and A_c are the angles within which light to the objective and from the condenser passes through P. B and B_c are equivalent to A and A_c, but relate to the whole field. C and C_c are the angles through which radiant energy can escape from P.

In microscopical studies, however, these potential sources of error are not so easily controlled. For reasonably high magnifications, the optical parts of a microscope need to be close to the object being observed. To justify a magnification of 250 diameters, for example, a microscope objective of any of the types that are currently manufactured needs to be within 4 to 6 mm of the preparation being studied. It covers a theoretical minimum angle of 29 degrees in any axial plane and cannot be allowed to get very much warmer than room temperature. Actually, the portion of the solid angle through which heat can leak by radiation, cones C

and C_c in Fig. 1, must be much larger than cone A of 29° diameter. Fig. 1 schematically illustrates a microscopical preparation and the apparatus for raising its temperature and for protecting the microscope lenses. Various zones in the solid angle surrounding the point P of the preparation are also shown. Of these, A and A_c represent the zones of light rays through P which must come from the microscope condenser and reach the objective if the point P is to be clearly portrayed in the microscopical image.* Since the field of a microscope always needs to be larger than a point, there is the circle surrounding P (an ellipse in the figure) through which pass the elements of B and B_c, parallel to the elements of A and A_c. There must be clear way for the light within these zones between the preparation and the lenses of the microscope. Therefore, the temperature-controlling devices and the shields for protecting the lenses from heat must not intrude upon the zones B and B_c. Radiant heat from P can escape along all directions within the zones C and C_c. Although in the case illustrated (representing approximately the conditions of a 10X objective) the zones A equal only about one-thirteenth of the total solid angle surrounding P, the zones C and C_c, representing the actual angle through which heat escapes, are between one-third and one-fourth of the total solid angle.

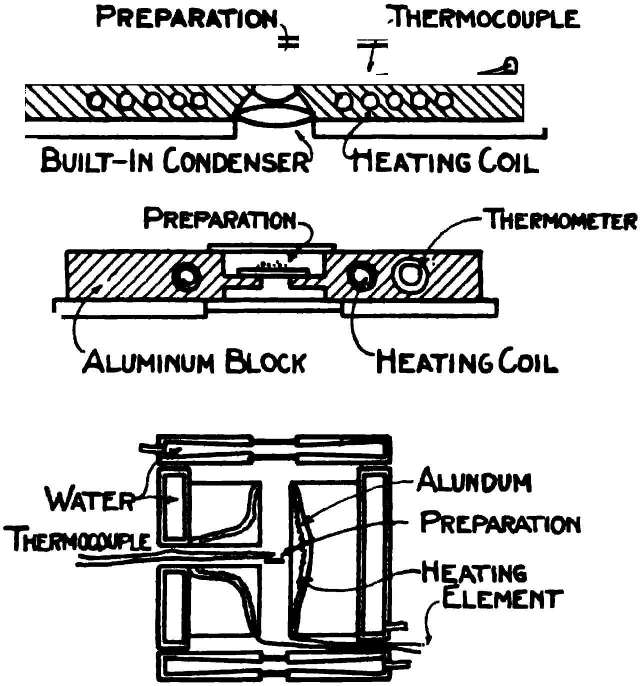

FIG. 2.
Three types of hot-stage.

It follows, therefore, that in real devices, particularly those which are used at high temperatures (temperatures at which heat is lost principally by radiation), heat flow into a preparation and out through the zones of illumination and observation becomes very rapid. I believe that one can feel assured that a temperature element is at the same temperature as a preparation only when there is the most intimate thermal contact between them. The thermoelement must be a real part of the preparation itself. This is impossible in practice with bulb or resistance thermometers because they are so large. With thermocouples, which are thus the only practicable thermometers, the wires must be of fine gages (to make them small and to decrease heat losses by conduction). Because of this fine gage, they require the use of potentiometers rather than millivoltmeters for dependable results.

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* Based upon the theories of numerical aperture and critical illumination.

There have been designs in which some attempt has been made, not to have the temperature-sensitive element a part of the preparation, but rather to have it in some way symmetrically placed with respect to it. Such are the hot stages of Klein,[4] Amdur and Hjort,[7] Kofler and Hilbck,[5] and, to some degree, a majority of the other devices that have been used. Several representative types are schematically illustrated in Fig. 2.

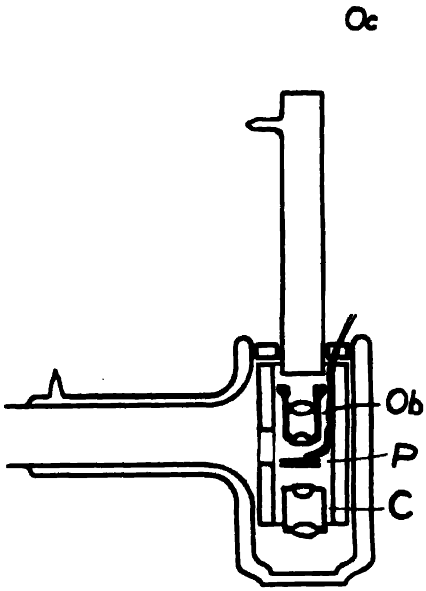

FIG. 3. A cold-stage with objective and condenser within the controlled space.

Here are represented the essential parts of the Leslie-Heuer apparatus. *Ob*, *Oc*, and *C* are the objective, ocular, and condenser. They are contained within a Dewar flask with plane windows at the bottom. Observation is through the evacuated long tube, *T*, with plane windows top and bottom. The cooling device surrounds the preparation, *P*, the thermocouple, the objective, and the condenser.

Low-Temperature Apparatus

When well-planned apparatus is used, the problem of securing uniform temperatures causes little trouble in cold-stage work—at least down to temperatures in the neighborhood of that of liquid air. Microscope objectives can be secured from several manufacturers which are not likely to be injured even by extremely low temperatures, provided such temperatures are not approached too quickly. Stirred liquids of relatively high heat capacity and low melting point may be used to surround preparations and may be placed very close to the lenses of a microscope. It is easy in such cases to prevent trouble from condensing water vapor simply by directing slow currents of dried air from a small nozzle against the windows through which a preparation is being observed, or even by wetting the windows with a thin film of glycerin. Condensers and objectives, protected only by glass caps, may dip directly into baths of controlled low temperatures. When cold, stirred gases are used to surround preparations, the condenser and objective can be immersed directly in the controlled space. A perfectly functioning apparatus of that type, which was described by Leslie and Heuer,[8] is schematically represented in Fig. 3. With devices of each of these types, the same arrangements for controlling and measuring temperature may be employed as are used in other fields.

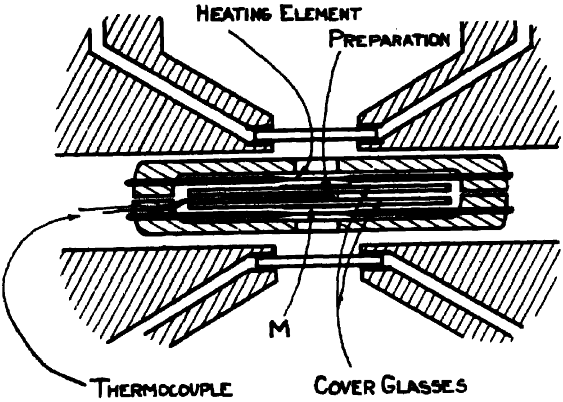

FIG. 4. Schematic representation of the central part of the Stadnichenko microscope furnace.

The scattered sample, between cover glasses, has a thermocouple at its midst. The heating element is designed to surround the preparation uniformly, as far as possible. The slight thickening of the top surface of the upper cover glass and the bottom surface of the lower cover glass are the positions *M* to which reefrence is made in the text.

Experiments to Locate the Source of Temperature Discrepancies in a Well Designed and Constructed Microscope Furnace

Miss Taisia Stadnichenko of the U. S. Geological Survey, in connection with her researches upon oil-shales and coal,[9] employed a microscope furnace in which conditions for the protection of lenses and the elimination of temperature differences between preparation and thermo-junction are as nearly perfect as seem possible. This apparatus has not yet been described in detail, but the essential parts are about as shown in Fig. 4. In this apparatus an attempt was made to complete, so far as possible, the sphere of uniform temperature around the preparation and to check convective currents of gas through the preparation. The thermometer element is in intimate contact with the sample.

The microscope furnace which was used in the present study was patterned upon Miss Stadnichenko's model, after about 80 different articles dealing with hot-stages had been consulted. It does not differ from hers except in unimportant details. In it, thermocouple wires of No. 36AWG lead to the center of the field of vision. Two slide-wire resistances in series are connected to the terminals of the 120-volt power supply and the leads to the heating element are connected, one to a slider and the other to the grounded terminal of the one resistance.

With this apparatus it seemed assured that differences in temperature between the preparation and the thermocouple would be negligible. This appeared even more probable when the first observations of melting-point were made, such as are illustrated in Fig. 5. The photomicrograph shows scattered fragments of potassium dichromate in the same field with the thermal junction. Each of the particles of salt—a sample of high purity, with a melting point of 397.5 °C—has been held partly melted and partly crystalline for five minutes. The particles lie practically in a plane with the thermal junction and some of them are much closer to the junction than many of the salt particles are to each other. When the temperature in such a run was slowly raised one-fourth degree, all the particles melted. Thus everything indicated that the temperature of the field was uniform within a small fraction of a degree. Yet, using a junction of previously calibrated Chromel-Alumel wires, the indicated melting point was 392.3 °C—more than 5 degrees low.

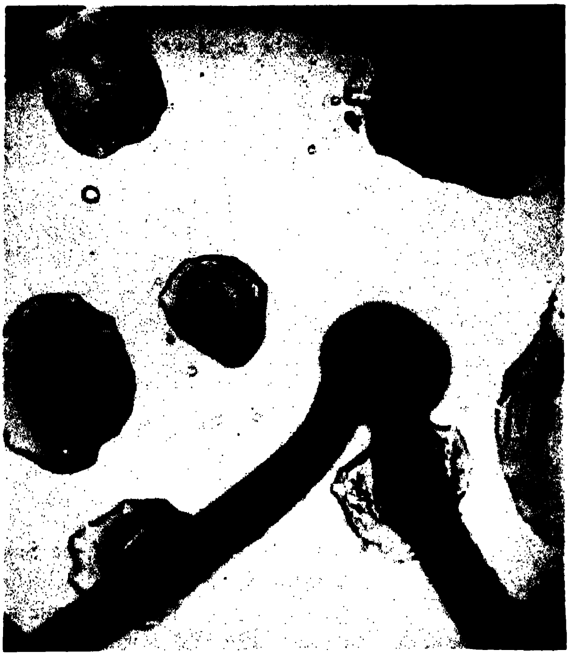

Fig. 5. A partly melted sample of pure potassium dichromate. ×50.

Each particle of salt has partly melted into contact with the cover glass. The thermal element, which is out of focus, is about 0.1 mm above the plane of focus (a distance equivalent to about 5 mm in the photomicrograph).

To secure further points in a calibration of this instrument the indicated melting temperatures of benzoic acid (NBS Standard Sample No. 39e, m.p. 122.35 °C) and sodium chloride (reagent grade, m.p. 804 °C) were used. In the determination with sodium chloride, it was necessary to replace the ordinary cover glasses of Fig. 4 with glasses of fused quartz, since the melting point of sodium chloride is well above the softening point of the cover glasses. In Fig. 6 indicated errors of the melting points are plotted against the true melting points of the reference compounds. The record conforms to the usual experience in which the discrepancies become larger with increasing departure from room temperature.

The sodium chloride, however, like the potassium dichromate, melted at the same temperature in all parts of the field. Since this threw doubt upon the easiest explanation of temperature errors in microscope heating stages—non-uniformity of temperature—there arose a desire to learn the real cause of the discrepancy. So began a search which in aftermath seems like taking some fantastic argosy on a quest for the obvious. Because it illustrates well the peculiar twists of this field, removed from the usual experience of physicists, the various theories that appeared and the experiments to test their validity are recounted in order.

The first thought was that conduction of heat along the thermocouple leads lowered the temperature of the junction. After winding the leads around in the heated region so that the length of immersion was five times as great as in the first experiments, the melting point observed for the potassium dichromate was still 392.3 °C.

It was supposed that radiation of electrons from the heating element might be causing an electrical asymmetry and influencing the measured potential. The terminals of the heating element were reversed and new melting-point determinations of potassium dichromate were made. Both alternating and direct currents were tried. In every case the temperature reading when the last bit of the crystal fragments melted was still a little more than 5° too low.

In a previous paragraph it was pointed out that there is very rapid transference of heat from the heating element into a preparation and out again. With the Stadnichenko type of apparatus that was used, a high temperature can be held very smoothly for a long time, but when the electric current is cut off it drops rapidly. As an example, it will fall from 900 °C to 100 °C in less than 2 minutes. So long as heat transfer to the preparation and away is by a single mechanism—radiation at one frequency, conduction, or convection—a steady state should be reached at which this heat "wind" ought not to maintain a temperature difference between a scattered sample of powdered salt and the tip of a thermocouple; but if conduction, convection, and radiation all participate, but to different degrees in heating and

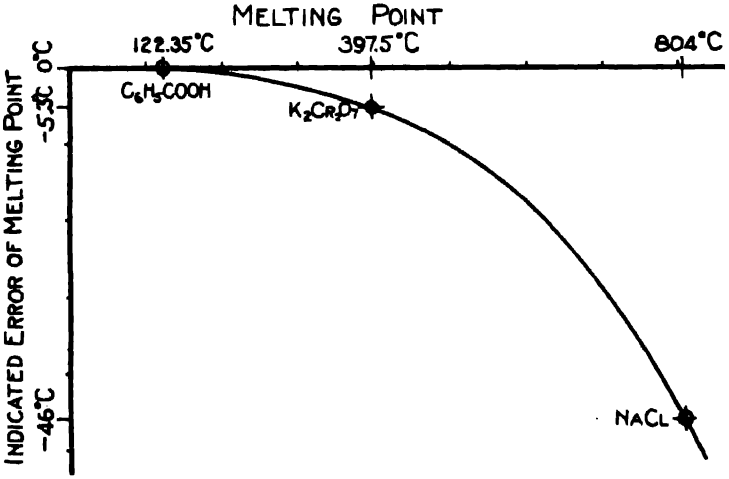

FIG. 6. Indicated errors of melting points.

cooling processes, than it seems reasonable that there might be such a spread as that found in the present experiments. Because of the higher temperature of the heating element it would be expected that, as compared with conduction or convection, radiation would be relatively more important in the heating than in the cooling of the preparation. If so, those materials which had higher absorption and emission coefficients would be at higher temperatures. Two possible methods of trying this theory seemed evident. (1) Evacuation of the system surrounding the preparation, thermocouple, and heating element ought to decrease heat changes by conduction and convection and so force both heat gains and losses to occur by radiation. Since both would be proportional to blackbody coefficients, thermocouple and sample should balance to about the same temperature. So far as their coefficients were dependent upon wave-length, differences would not be entirely eliminated. (2) The formation of a nearly complete metal mirror at the planes *M* in Fig. 4 should almost eliminate the effects of radiation and decrease the temperature difference between the preparation and the thermocouple.

A related explanation of the temperature discrepancy was that the cover glasses had absorbed radiant heat and so reached temperatures higher than the material between them. Since the test sample by melting could achieve better thermal contact with the glass, it would reach higher temperatures than the thermal junctions. It was decided that if this explanation was correct, the mirror technic should decrease the temperature error and that evacuation should be without effect.

To test the theories of the last two paragraphs, platinum mirrors were formed upon the cover glasses in the positions of *M* and *M* (Fig. 4). They were sufficiently dense that with a tungsten-arc lamp as illuminator, the field had normal brightness for visual work. The melting point of pure potassium dichromate was again determined. It was still only a little higher than 392 °C. Thus two theories were shown to be incorrect by one bracketing experiment.

The abrupt failure of the foregoing theories to explain the observed temperature errors was discomforting until it was recalled that 400 °C is reasonably high in the history of ordinary glass. Thus a little sintering might be expected at the point of contact between the salt fragments and the cover glasses. Below the melting point of the salt and the softening range of the glass, alkalies might yet be extracted from the glass and form with the salt a solution of conspicuously lower melting point. This would foster more extraction from the glass, so that what appeared to be a melting point would be, in fact, only a point upon a solidus curve. A new melting-point determination was made with polished fused quartz cover glasses * instead of the ordinary cover glasses. *The melting point of potassium dichromate as determined was now 397.6° C.*

If the extraction of alkalies from the glass had really been the cause of all the trouble, then the apparent melting point should be dependent upon the cover glass chosen. Cover glasses were selected from different sources. All were carefully washed by a rigid technic and the melting point of potassium dichromate determined with each of them. The melting points, using fragments from the inner part of the same crystal, ranged from 388 to 393 °C, the temperature being characteristic of the batch from which each cover glass was taken. The cover glasses were found to be slightly pitted at the spots where crystals of the salt had melted. That on which the lowest melting point was observed was the most deeply pitted.

The experiment with sodium chloride was repeated, with a piece of platinum foil as the support for the crystal fragments instead of the fused quartz cover glass (the top glass was not changed), and with vertical illumination. The observed melting point was 802.6 °C, less than 2° below the true melting point, instead of more than 45° too low as found on the quartz support. When quartz supports that had been used were examined, it was found that there was a curious sort of blistering that did not entirely wash off with water. It was as though sodium silicate had formed and again decomposed, leaving an expanded silica gel.

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* It should be pointed out that Miss Stadnichenko used fused quartz cover glasses in her experiments (see reference 9).

Thus it turned out that, in the present experiments, temperature measurements had been right all along. The trouble had been simply that soda-lime glass is not a satisfactory support for salts melting near 400 °C any more than quartz glass is for those melting near 800 °C. Although the trouble in this study had not been, as at first suspected, a lack of temperature uniformity, the precautions taken to secure it had not been unnecessary. Without them even larger errors, such as have been the usual experience with hot-stages, would have resulted. In critical experiments with microscope hot-stages, all precautions that are possible must be utilized. It is more troublesome to have thermocouples stick into a preparation than to have them safely immersed in some niche removed from actual manipulations. It may add several minutes to the time required for a melting point determination, but, when trustworthiness of temperature measurement is of first importance, it is wisest to make the tip of a thermocouple as intimate a part as it can be of the material which is being examined. The distribution and transfer of heat within and around the zone of observations must be controlled with all care. And even then it is best in this comparatively untrodden field to be always ready for new difficulties, even those that come from unexpected quarters.

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Smithsonian Temperature Measurements

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As the successors of Dr. S. P. Langley, we make regular daily use of the bolometer at our three field stations to measure the heating effects of the solar spectrum. We insert the bolometers in highly evacuated glass flasks of about a liter capacity. A cross-tube is inserted at right angles into the neck, and sealed at front and back by optically flat glass windows. The two vertical bolometer strips are soldered to insulated copper plates formed upon a copper tube inserted in the neck of the flask before evacuation. Three lugs project, which we solder to three platinum pins sealed into the glass neck. The copper tube is cut through, so that the bolometer strips can be observed from the back with a long-focus eye-piece, and so that one of the bolometer strips is exposed from in front to the solar spectrum. The bolometer strips are of thin platinum, flattened while within the silver sheath of the so-called Wollaston wire. The strips are about 15 mm long, 0.1 mm wide, and of approximately 4 ohms resistance. They are blackened by smoking over burning camphor. Two balancing coils of manganin, of about 50 ohms resistance each, are soldered to two of the platinum pins on the outside of the neck of the flask, to form a Wheatstone bridge. The bridge is balanced by a variable resistance of several thousand ohms shunted about one of the manganin coils. We find these bolometers admirably adapted for making self-recording traces of the intensity of energy in the solar spectrum. As used in the field, with an astatic reflecting galvanometer, of about 10 ohms resistance and 3 seconds complete period, a deflection of a millimeter on the scale at 1.5 meters corresponds to about one millionth of a degree in average rise of temperature of the bolometer strip. The galvanometer is usually disconnected at night, but its zero reading remains constant to within one or two cm on the scale for weeks at a time. The photographic record rarely shows accidental wiggles as great as 1 mm in amplitude.

Several attempts have been made by us to measure the distribution of radiant energy in the spectra of the brighter stars with the aid of the 100-inch telescope at Mount Wilson. In the year 1928 I built for this purpose a radiometer system weighing about 0.9 mg. The vanes were made of the wings of the housefly. They were 0.4 mm wide, 1.0 mm tall, and separated 1.2 mm between centers. Each vane was triple, comprising a front lamina blackened with lampblack paint, and two separated laminae in its rear. The system was suspended by a quartz fiber about 15 cm long, and so fine that when the system was hung in air at atmospheric pressure, the upper end of the fiber could be twisted 45 times before any response of turning was seen at the vanes. As used, the system was hung within a fused quartz tube about 4 cm in diameter, which was optically ground and polished opposite the radiometer system, so that radiant energy could enter, and the mirror of the system could be observed from any azimuth. When pure hydrogen gas at a pressure of 0.23 mm of mercury surrounded the system it showed, when first constructed, a complete period of 24 seconds. But I foolishly cleaned the quartz tube in the usual manner with alcohol and chamois skin to take off finger marks. It then became electrified, and the complete period of swing fell to less than 1 second. After several days it was up to nearly 3 seconds for a complete period, and was used in that condition for stellar observations. The deflections could be observed on a scale at 6 meters when as small as 0.03 mm. A candle at 2.4 meters, with one silver reflection and three plates of thin glass or quartz interposed, gave a deflection of 80 mm on a scale at 0.4 meter. Had the original 24-second complete period been available, the sensitiveness would have been fully 50 times as great, and the steadiness almost as satisfactory.

In the year 1938, we tried another approach on the energy spectra of the stars. Nearly 20 years ago the late Dr. Elihu Thomson prepared for us a special magnetic shield for the galvanometer, comprising 15 concentric iron cylinders, each about 2 mm thick, and separated by layers of plaster of paris, each about 5 mm thick. The inner cylinder is about 3 cm in diameter and the outer one about 20 cm. They are all of them about 20 cm long. There is no side opening in the shield, for we designed to reflect a beam of light down the axis to the instrument for reading purposes. Our Mr. Wm. H. Hoover constructed a 4-coil astatic galvanometer of 16.5 ohms total resistance to be inserted in this shield. The coils, wound after the form preferred by Maxwell's theory, were only about 1.2 cm in outside diameter, and were spaced very near together. Thus the two groups of magnets of the astatic needle system (built of fine tungsten-steel wires only about 1 mm in length) were so near together that, even when they were not shielded, magnetic changes produced but little effect. Within the shield the system was so far immune to magnetic influences from without that it was very difficult to control. However, with strong magnets above and below, we could raise the time of single swing to 10 seconds when the tubular glass case (which surrounded the galvanometer but not the shield) was highly evacuated. Under these circumstances the system was so steady that accidental deflections exceeding 1 mm were rarely observed on a scale at 5 meters. Currents of 10^{-13} ampere could be measured.

This galvanometer was connected to a vacuum thermopile, in focus of selected regions of wave-lengths in the stellar spectrum. We used 10 special Christiansen filters to select the desired wave-lengths. They isolated regions averaging about 100 angstroms in width, narrower in the ultraviolet, wider in the upper infrared. When the thermopile was connected, Mr. Hoover was unable to get sufficient steadiness. He therefore did not use the full available sensitivity of the galvanometer, but contented himself with a complete period of 4 seconds. Under these circumstances he observed in the spectrum of the star Vega deflections of 20 mm on the scale at 5 meters. With improved conditions we hope to repeat the work in 1942 with the 200-inch telescope. We expect to be able then to get continuous registration of stellar spectra to the third magnitude, using a diffraction grating.

In Mr. Hoover's stellar measurements and in the extensive quantitative investigations of photosynthesis in the higher plant forms which are going on in the Smithsonian Division of Radiation and Organisms, highly sensitive, quick-responding thermoelectric elements by Mr. L. B. Clark have been used. In some of these instruments a blackened receiver 1 mm in diameter and 0.0013 mm thick is welded to each of the junctions of dissimilar wires. The couple is within a sealed enclosure permanently evacuated to a pressure measured by less than 10^{-4} millimeter of mercury. In this way the sensitiveness is increased from 20- to 30-fold above that found in atmospheric pressure. The wires are not of the bismuth-tin alloys so frequently used for highly sensitive thermocouples, but are of a special mixture of chromium, cobalt, and nickel. Although reduced in diameter uniformly by a special and secret process to a diameter of about 0.004 mm, so that their resistance ordinarily ranges from 40 to 50 ohms per centimeter, they are extremely rugged, so that quite severe jolts and moderate bendings do not break them. The emf of the negative wire is 38 microvolts per ° C against lead, the positive wire not quite so much. The couple gives about 3.3 microvolts per microwatt of radiant energy per square millimeter. In some housings the windows are of glass so thin (0.025 to 0.050 mm in thickness) that it is sucked back into a cup-shaped form on evacuation. Such bubble windows are available to transmit radiant energy freely between 2500 and 65,000 angstroms. So small is the capacity for heat of the thermocouples that they reach a full response within less than one second.

Temperature Distribution and Heat Flux in Air by Interferometry

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I. Introduction

One of the most common and most important types of heat transfer is that which takes place between a solid surface and the air in contact with it. As examples one may mention the hot-water and steam radiators in a house, the radiator in an automobile, the cooling fins on an airplane engine, and the heat transfer from the warm air of a room to a cool pane of window glass, and its transfer again from the glass to the still colder air outside.

In the past forty years many attempts have been made at a theoretical solution of this problem. A complete mathematical solution must combine the hydrodynamic laws for the motion of a viscous fluid in both laminar and turbulent flow with Fourier's laws of heat conduction. Because of the extreme complexity of the problem no complete solution has as yet been made.

To avoid the mathematical difficulties involved in the analysis of turbulent flow, the first approximation is to consider the problem as involving laminar flow only. The combination of the laws of laminar flow and heat conduction is further simplified by assuming a non-viscous fluid. This method was followed by Boussinesq[1] and Russel.[2] The calculated results differ widely from those observed experimentally, and the method is of little value in the direct calculation of heat transfer.

The method of dimensional analysis[3,4,5,6] has been of great value in extending the use of experimental data on convective heat transfer to conditions not specifically covered by experiment. It does not however indicate what takes place in the boundary region between the solid and the fluid.

In calculating the heat transfer by convection it is generally assumed that the heat is transferred by conduction through a thin film of fluid in contact with the solid. It is assumed that on one side of this film the temperature is that of the solid, and on the other side it is that of the fluid at a great distance. The thickness of such a film may be calculated from measurements of (a) the convective heat transfer, (b) the total temperature drop and (c) the average thermal conductivity of the fluid. Since the conducting film as defined in this manner is idealized, it is the practice to combine the thickness of the film and the thermal conductivity into a film coefficient.[7] These film coefficients, or coefficients of heat transfer, have been determined over a wide variety of experimental conditions and can be adapted to a particular problem by the method of dimensional analysis.

The film hypothesis was placed on a theoretical basis by Langmuir.[8] He assumed that near the surface the flow would be laminar, with the velocity increasing from zero at the surface to a maximum critical value, at which point the flow would break into turbulent motion. Because of this turbulence it was assumed that the temperature in this turbulent region would be the same as that of the ambient fluid at a great distance. This theory then leads to the conclusion that the temperature drop will be confined to the region of laminar flow. Formulas for the thickness of the film were deduced from the kinetic theory of gases, taking into consideration in particular the variation with temperature of the thermal conductivity and the viscosity. From these formulas it was possible to correlate the observations of many observers on the convective heat transfer for wires and cylinders in different gases. The correlation was remarkably good over a wide range of pressures and temperatures of the gas and of cylinder diameter.

In order to determine how closely the film theories agree with the physical facts, it is necessary to measure the temperature and the velocity distribution in the gas near the hot surface. Griffith and Davis[9] made such an investigation for free convection in air in front of a vertical hot plate. Similar studies have been made for forced convection. In such investigations the air velocities are measured with a hot-wire anemometer or by the deflection of quartz fibers, and the temperatures by the resistance of a fine platinum wire or by thermocouples.

Certain considerations will indicate the objections to the use of any material thermometric device for the measurement of the temperature in these thin air films. In natural convection a temperature gradient of about 200 °C per cm will exist in the film of air adjacent to a vertical hot-plate which is maintained at a temperature of 100 °C above the room air. In such a temperature gradient, conduction along the leads of the thermometer and change in the air flow are likely to cause the temperature of the thermometer to differ by many degrees from that of the air at that place in the absence of the thermometer.

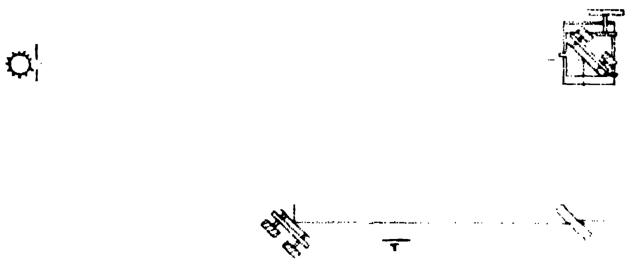


Fig. 1. Plan of the apparatus.

The effect of radiation is also important. It may readily be shown, by alternately shielding and exposing the bulb of a mercury thermometer to radiant energy, that the temperature of the thermometer, when exposed, may differ by several degrees from that of the air which it is supposed to measure. Experiments by the author have shown that the effect is much less with a brightly polished thermocouple than with the same thermocouple covered with lampblack. It is, however, an effect which cannot be eliminated except by shielding. This is not possible in measuring the temperature distribution in air at points less than a millimeter apart. The best that can be expected of any material thermometer is that it will measure its own temperature correctly. Certain conditions are necessary if the temperature of the thermometer is to be the same as that of the medium in which it is immersed. These conditions cannot be met in the film of air near heated surfaces.

II. Procedures Using the Interferometer

The use of any material thermometer may be avoided if the air can be made to reveal its own temperature. This is made possible by the effect that a change in temperature has on the index of refraction of the air. The change in the index of refraction can be measured with great precision by means of an interferometer.

The general arrangement of the apparatus is shown in Fig. 1. The interferometer designed by Zender[10] and Mach[11] was chosen for this purpose. This interferometer is a modification of the instrument designed by Jamin[12] for the measurement of the index of refraction of gases. The light from a mercury lamp, passing through a 10-mm aperture, is brought to a slightly convergent beam by two condensing lenses. The use of two lenses is found convenient, as the focal length of the combination can be varied by moving the inner lens without moving the lamp or the large outer lens. The lamp and lens are housed in a light-tight cabinet separated from the interferometer by a 60-cm tube. At the end of the tube is a shutter so that the light of the lamp may be completely cut off.

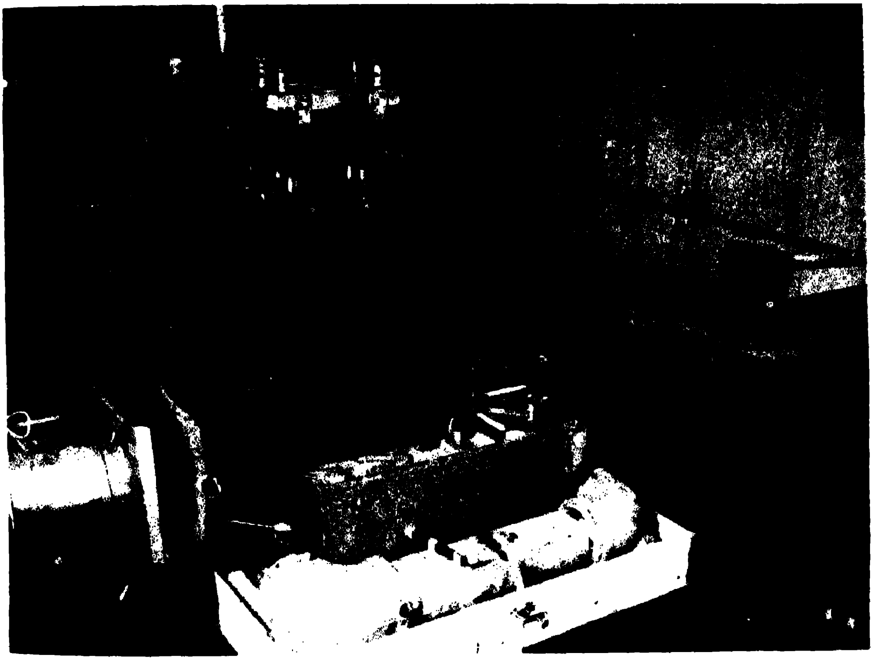


FIG. 2. Photograph of the interferometer.

Before entering the interferometer, the light passes through a Wratten 77 filter which will transmit only the mercury green light. The heated body, *H*, is placed in one arm of the interferometer as shown in the figure. The instrument is adjusted so that the beam of light is parallel to the heated surface and both accurately coincide with the axis of the interferometer. The fringes were brought to a virtual focus at the end of the hot body nearest the camera (line *A A*), except in the case of the hot-wire, when they were brought to a focus at the middle of the wire. The camera has a length from lens to plate of 136 cm. A 2¼ diopter spectacle lens was used for the objective, giving a magnification of 2.4 diameters. Enlargements made from the negatives give a total magnification of 7 diameters. After the exposure has been made for the fringes, the light from the mercury lamp is cut off and a millimeter scale is placed in the focal plane and an exposure made on the same plate by white

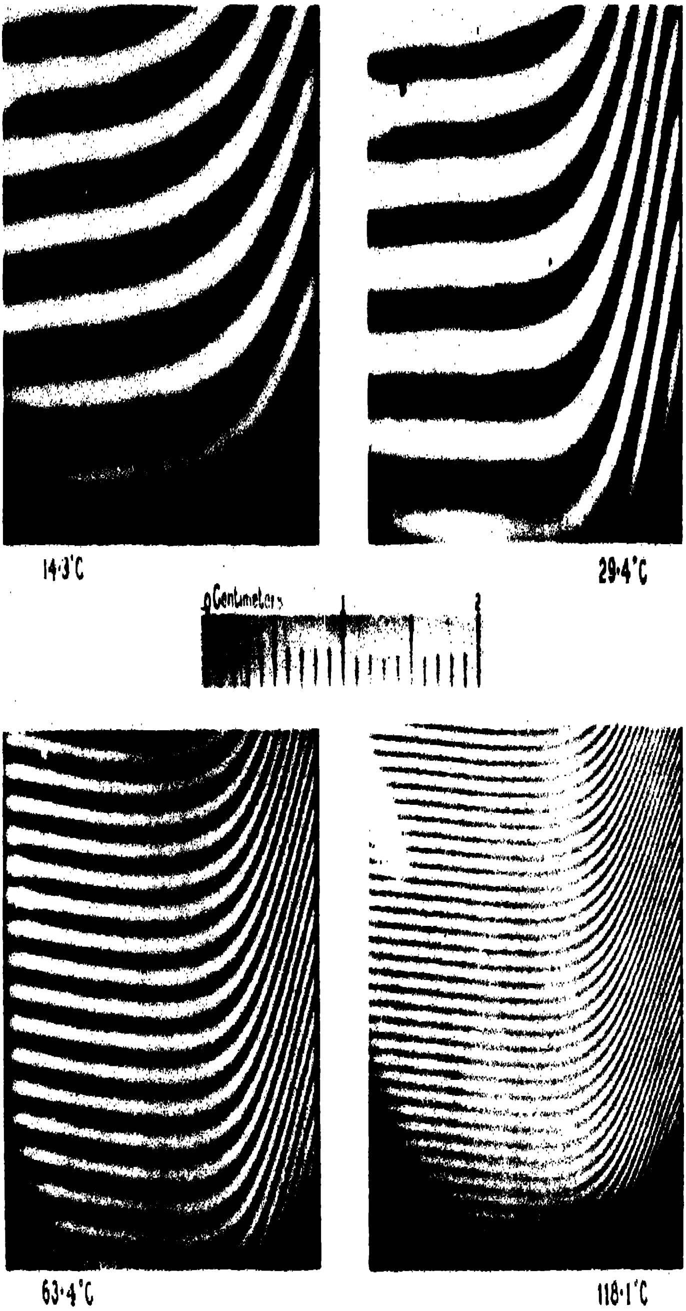


Fig. 3.

Fringes in front of a vertical heated plate for the values of the temperature rise indicated.

light. The image of this scale is used in locating the position of the air temperatures which are determined by the shift in the interference fringes.

Fig. 2 shows a photograph of the interferometer. The frame is a two-inch iron pipe through which water at room temperature is allowed to flow. The frame rests on sand in a shallow trough supported on an open framework, thus avoiding any convection currents due to chimney effects. Two parallel plates are shown suspended in the proper place for the photography of the interference fringes about the lower portion of these plates. At the extreme left is the tube through which the light is led from the lamp house. At the right is shown the objective end of the camera with the diaphragm for the different stops. The shutter is setting on top of the camera. In use it drops over the lens and the exposure is made by rotating the handle. The camera was replaced by a telescope in making adjustments.

Four photographs showing the fringe displacement in front of a vertical hot-plate are shown in Fig. 3. In each photograph the edge of the hot-plate is seen at the extreme right. This plate was 21 cm high and 10.3 cm wide. The center of the photograph is 10.5 cm from the bottom of the plate. The difference between the temperature of room air and that of the hot-plate is given with each figure. The photograph of the millimeter scale was obtained by a double exposure on one of the photographs of the fringes, all of which are enlarged to the same scale. In the first two photographs the instrument has been adjusted for wide fringes so as to get an adequate fringe shift for the purpose of measurement. In the third and fourth photographs the fringes have been made much narrower, so as to get the full fringe displacement on the plate. In every case the fringes would have been straight across if it were not for the fact that the light in one arm of the interferometer passed through air of varying index of refraction.

III. Calculation of Results

1. General. Let *A* and *B* (Fig. 4) be the center lines of two adjacent interference fringes formed in the column of heated air in front of a vertical heated surface. At the point *P* there has been a shift of a whole fringe width of the center line of the fringe *B*. This indicates that, because of the higher temperature and consequently lower index of refraction of the air, the light through *P* contains one less wave of light than the light through *Q*.

The temperature of the air is derived from its density which is related to the refractive index by the Lorenz-Lorentz [13] equation

$$\frac{n^2 - 1}{n^2 + 1} = C\rho \tag{1}$$

where n is the index of refraction, ρ the density, and C a constant characteristic of the fluid.

Since the index of refraction of air under room conditions is of the order of 1.0003, the equation above reduces very closely to

$$(n - 1) = 3/2\ C\rho \tag{2}$$

If n_1 is the index of refraction of the room air and n_2 the index of refraction of the heated air in front of the plate, and ρ_1 and ρ_2 are the corresponding densities, then

$$\begin{aligned}(n_1 - n_2) &= 3/2\ C\,(\rho_1 - \rho_2)\\ &= 3/2C\rho_1\left(1 - \frac{\rho_2}{\rho_1}\right)\\ &= (n_1 - 1)\left(1 - \frac{\rho_2}{\rho_1}\right)\end{aligned} \tag{3}$$

If L is the length of the path of light under consideration, which is that of the heated surface plus a small end correction, and if λ_0 is the wave-length in vacuum of the light used, then the number of wave-lengths, N_0, along this path in vacuum would be

$$N_0 \quad L \tag{4}$$

If N_1 and N_2 are the number of wave-lengths under the actual conditions, then the index of refraction is given by

$$n_1 = \frac{N_1}{N_0} \tag{5}$$

and

$$n_2 = \frac{N_2}{N_0}$$

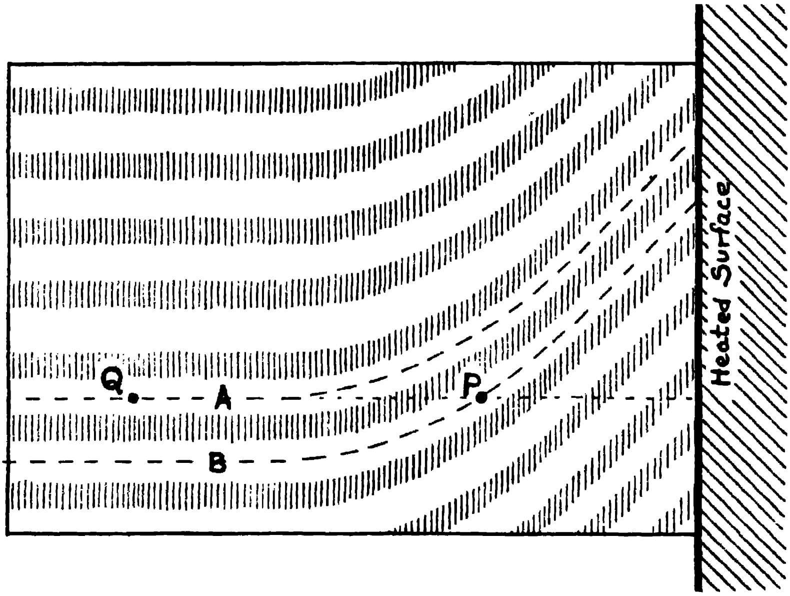


FIG. 4. Method of measuring the air temperature from the fringe shift.

Inserting the values of (4) and (5) in Equation (3) and rearranging yields

$$(N_1 - N_2) = (n_1 - 1)\frac{L}{\lambda_0}\left(1 - \frac{\rho_2}{\rho_1}\right) \tag{6}$$

On applying the gas law, and representing $(N_1 - N_2)$ by ΔN, this becomes

$$\Delta N = (n_1 - 1)\frac{L}{\lambda_0}\left(\frac{T_2 - T_1}{T_2}\right) \tag{7}$$

On solving explicitly for the temperature rise above that of room air this equation becomes

$$T_2 - T_1 = T_1 \cdot \frac{\Delta N}{(n_1 - 1)\frac{L}{\lambda_0} - \Delta N} \tag{8}$$

Since ΔN is equal to the fringe displacement as measured in fringe widths, Equation (8) can be used to measure the temperature rise above room air at any point along the center line of an interference fringe. T_1 is the temperature of the room air in degrees Kelvin and the quantity $(n_1 - 1)$ is given in the "International Critical Tables" [14] for standard conditions and may be calculated for any conditions by using the gas laws, making proper correction for humidity.

2. End Correction. As previously mentioned, the length L includes the length of the heated surface plus a small correction, ΔL, which takes into account the fact that the layer of heated air extends beyond the ends of the hot surface. It was found that, when no allowance was made for this end correction, the temperature rise for the air at the surface of the plate was greater by 5 per cent than the temperature rise to the plate itself. By making $\Delta L = 5$ mm for a 100-mm plate the calculated temperature of the air in contact with the plate is made the same as that of the plate itself. This value holds for all four plates as follows:

Observed (°C)	Calculated (°C)
118.1	118.9
63.5	63.8
29.4	29.4
14.3	14.3

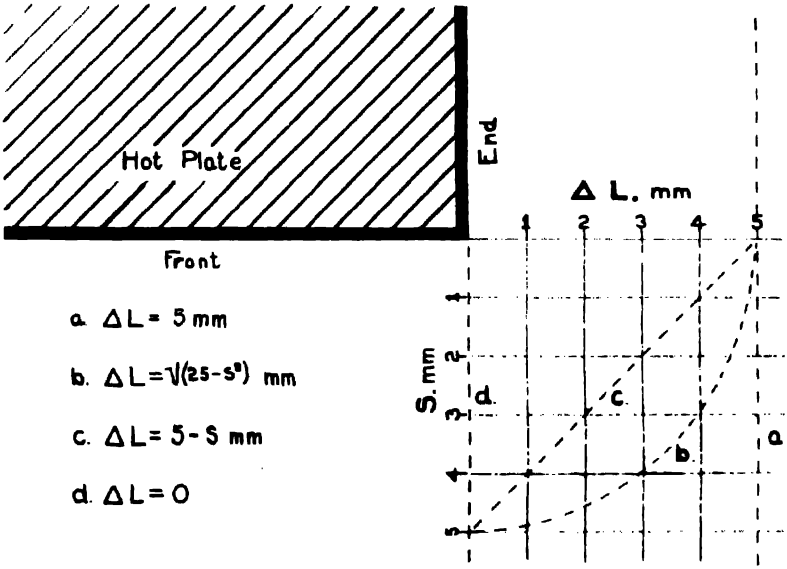


Fig. 5. Possible assumptions as to the end correction.

Having determined the value of ΔL at the surface of the plate there remains the problem of determining its approximate value at any point at a distance, S, in front of the plate. As the quantity involved is small, a purely empirical solution was considered sufficient. In Fig. 5 are shown some of the possible assumptions. One may assume (a) that ΔL remains constant throughout this region, or (c) that ΔL decreases linearly to zero at some point, say for convenience 5 mm in front of the plate. Between these two limits a circle (b) has been drawn. For any distance, S, from the surface of the plate, ΔL was chosen as the corresponding semi-

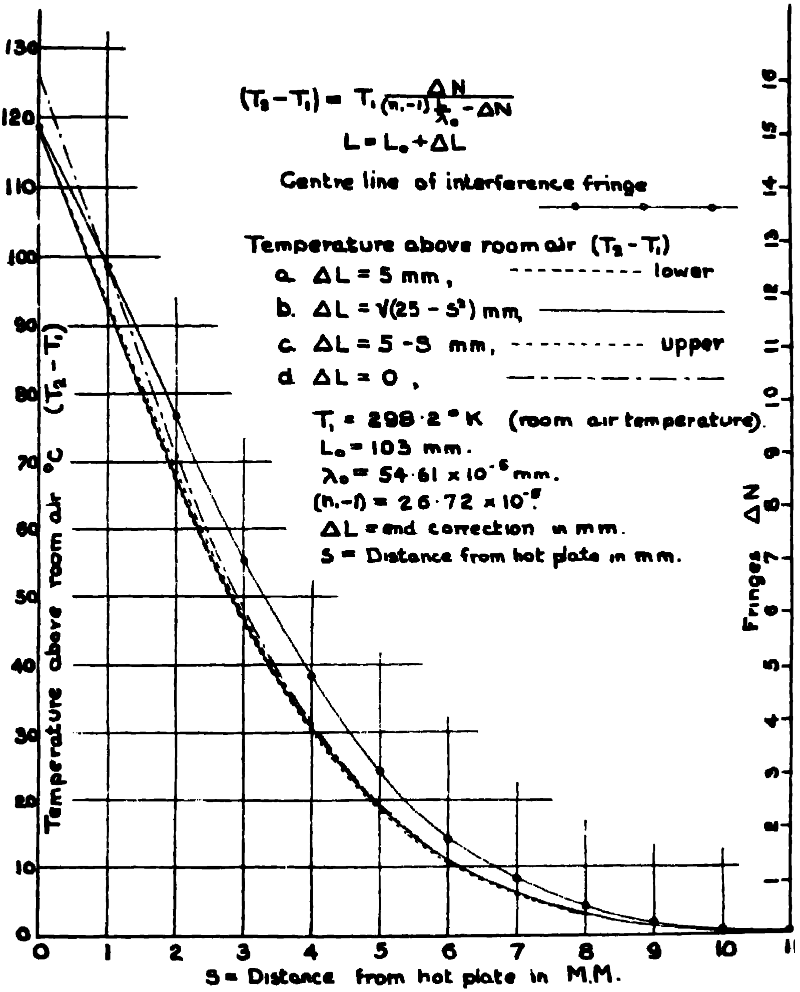


FIG. 6. Air temperatures as calculated from the fringe shift.

chord of this circle. Fig. 6 shows the displacement of the center line of an interference fringe for a total temperature rise of 118.1 °C. Below this are shown four curves giving the corresponding temperatures as calculated for four assumptions for the end corrections.

3. Effect of Aberration. Another factor that needs to be considered is that the light passing by the heated surface is not homogeneous in direction. The reasons for this are that the light source is not a point but a disk one centimeter in diameter, and that the lens system is not free from spherical aberration. As a result, some of the rays through a given point in the focal plane will have come through regions of air at a lower average temperature than that corresponding to the point in question, and some through air at a higher average temperature.

At a distance from the plate these effects are likely to balance and no appreciable error will result. Furthermore, the effect can be reduced by using a small aperture in front of the camera lens. With a 3-mm aperture, with the focus set on the nearest edge of the plate, the cone of light entering the lens from a point in the focal plane will have a diameter at the far edge of the plate of 0.55 mm. However a 3-mm aperture required an exposure of 20 seconds and many plates were

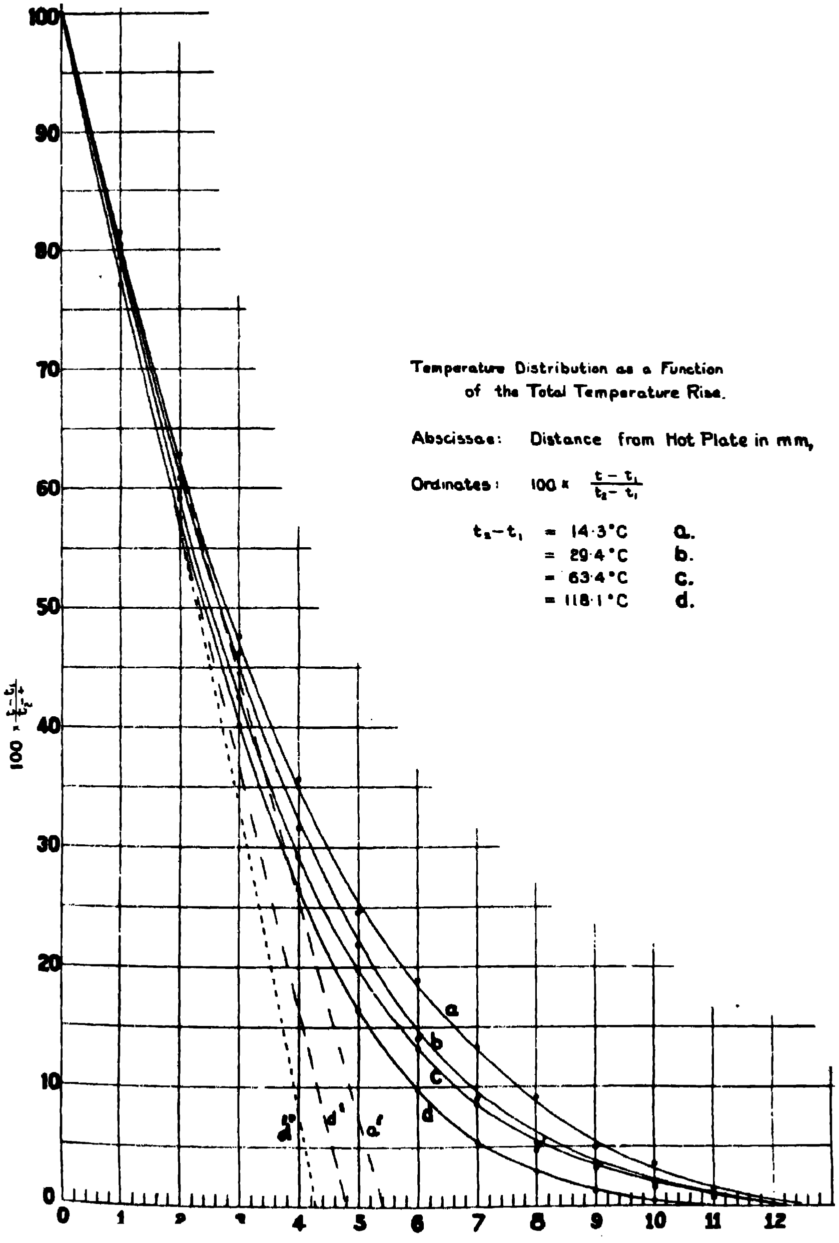


Fig. 7. The effect of temperature rise on temperature distribution.

spoiled by stray air currents which caused the fringes to move. In practice a 6-mm aperture was used, increasing slightly the aberration error.

At the surface of the heated plate the effect will be greatest. It may be shown, for a 3-mm aperture, that the temperature as measured at the surface corresponds in fact to that at a distance 0.12 mm out from the surface. This calculation is based on the assumption that all rays within the half cone are equally probable, and an average is taken of each ray over its full length across the plate.

It should be noted that the purely empirical method used in making the end correction tends also to correct small errors due to aberration and imperfect collimation.

IV. Experimental Results

1. The Single Vertical Plate. The relative temperature distribution in the air in front of a vertical hot plate is shown in Fig. 7. The four curves correspond to the four photographs shown in Fig. 3. Curves *a'* and *d'* are straight lines tangent to curves *a* and *d* at the upper portion near the plate. They indicate that the temperature gradient is not only absolutely, but proportionately greater with increase in temperature rise. The coefficient of proportional temperature gradient is found to be +0.12 per cent per degree of total temperature rise. The curve *d''* shows the temperature distribution under the conditions assumed in the film theory, taking into consideration the variation of the conductivity with the temperature. Curve *d* shows the actual temperature distribution for the same temperature rise as measured in the interferometer.

2. Convective Heat Transfer. The convective heat transfer per unit area may be calculated from the temperature gradient at the surface of the plate, and the thermal conductivity of air at the plate temperature.

$$Q = -K\frac{dT}{dx} \tag{9}$$

For a temperature rise of 118.1 °C with the plate at 143.3 °C

$$K = 0.000308 \text{ watt cm}^{-1}\,{}^\circ\text{C}^{-1}$$

$$\frac{dT}{dx} = -246\ {}^\circ\text{C cm}^{-1}$$

whence

$$Q = 0.076 \text{ watt cm}^{-2}$$

For a temperature rise of 14.3 °C with the plate at 36.8 °C

$$K = 0.000246 \text{ watt cm}^{-1}\,{}^\circ\text{C}^{-1}$$

$$\frac{dT}{dx} = -27\ {}^\circ\text{C cm}^{-1}$$

whence

$$Q = 0.00666 \text{ watt cm}^{-2}$$

When the heat flux is expressed in terms of the temperature rise we may assume that

$$\frac{Q_1}{Q_2} = \left(\frac{\Delta T_1}{\Delta T_2}\right)^n \tag{10}$$

where *n* is found to be 1.17 and not 1.25, as generally assumed. This value agrees, however, with that obtained experimentally by Griffith and Davis[9] and with that calculated by Vernotte.[15] Their values are derived from total heat input, whereas the values obtained by measurement of the interference fringes apply to the particular portion photographed.

The convective heat flux can also be determined from the slope of the interference fringe at the surface of the plate. If the fringes are adjusted to be perpendicular to the plate when cold, the heat flux from any point on the heated plate is given by

$$Q = \frac{K_s \lambda_0 B_s}{(n_s - 1)LB} \frac{T^{2.76}}{T_s^{1.76}} \frac{N}{y} \tan\theta \tag{11}$$

where Q = heat flux in watts cm^{-1};
K_s = thermal conductivity of the air at standard pressure and temperature;
λ_0 = the wave-length of light in vacuum;
B_s = the standard barometric pressure;
n_s = the index of refraction of air at standard pressure and temperature;
L = the width of the plate plus the small end correction;
T_s = 273.2 °K, standard temperature;
T = the temperature of the plate;
B = the existing barometric pressure;
$\frac{N}{y}$ = number of fringes per cm in room temperature air;
$\tan\theta$ = the slope of the interference fringe at the plate surface.

While Equation (11) appears complicated, it is in fact simple to use, as all quantities except the last can be included in a single constant. This equation is obtained from the derivative of Equation (7) giving

$$\frac{dN}{dx} = (n - 1)\frac{L}{\lambda_0}\frac{1}{T}\frac{dT}{dx} \tag{12}$$

Solving explicitly for the temperature gradient in the air at the surface of the plate, and substituting $\frac{N}{y}\tan\theta$ for $\frac{dN}{dx}$ gives

$$\frac{dT}{dx} = -\frac{\lambda_0 T}{(n - 1)L}\frac{N}{y}\tan\theta \tag{13}$$

The quantity $(n - 1)$ varies according to the general gas law so that

$$(n - 1) = (n_s - 1)\frac{B}{B_s}\cdot\frac{T_s}{T} \tag{14}$$

The convective heat flux for laminar flow is given by

$$Q = -K\frac{dT}{dx} \tag{9}$$

According to the classical kinetic theory, the thermal conductivity and the viscosity should be proportional[16, 17, 18] to $T^{1/2}$. However, experimental data differ widely from the predicted results. The experimental data of Euken[19] fit quite closely the equation

$$\frac{K_2}{K_1} = \left(\frac{T_2}{T_1}\right)^{0.76} \tag{15}$$

Equation (11) is then obtained by the substitution of Equations (13), (14), and (15) in Equation (9).

The above figure for the exponent should, however, be taken with caution, as more recent measurements on the conductivity of air by Gregory and Archer,[20] and others[21, 22, 23] give results that are ten per cent higher than Euken's and in which

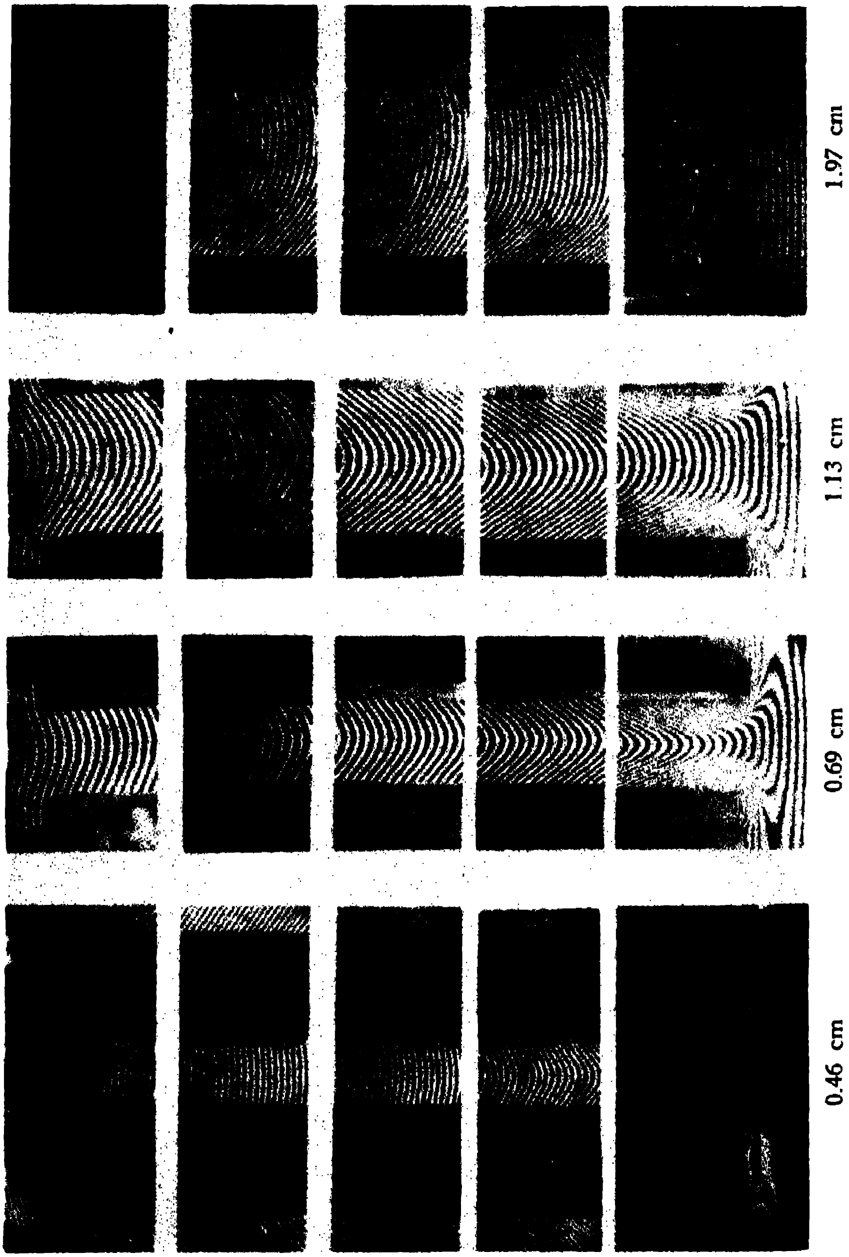


FIG. 8. Representative photographs of the interference fringes between two vertical parallel plates heated to the same temperature for the spacings indicated above.

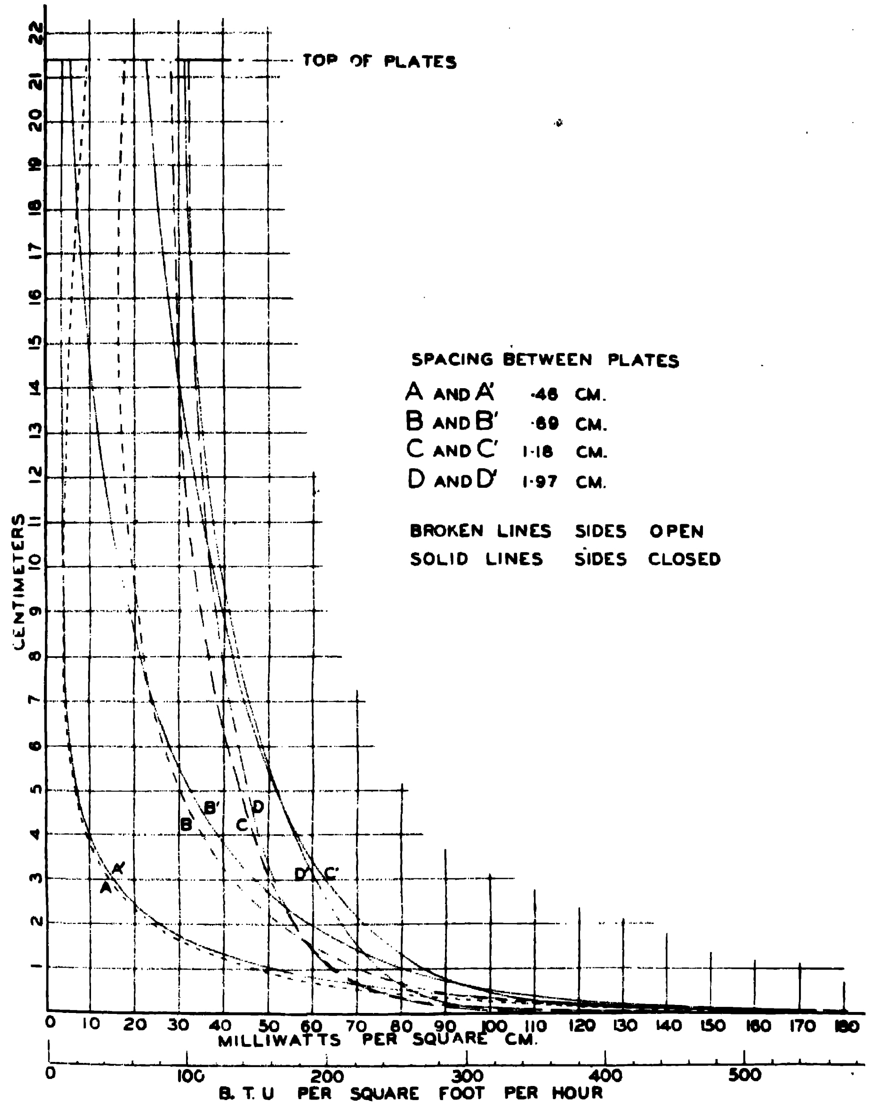


FIG. 9. Convective heat flux from one of two vertical parallel plates.

K varies more nearly as $T^{0.85}$ than as $T^{0.76}$. These differences will affect the determination of the absolute value of the heat flux, but they will not affect the relative value of the heat flux from point to point on the plate, which was the purpose for which Equation (11) was derived.

3. **Vertical Parallel Plates.** Photographs were taken of the interference fringes between two vertical parallel plates for four different spacings between the plates. Representative samples of these photographs are shown in Fig. 8. From the slope of the interference fringe the convective heat flux was determined from point to point up the inner surface of one of these plates. In each case the optical

axis lies along the inner surface of the left plate. In the photographs shown, the space between the plates was open on the sides as well as on the bottom and top. A second set was then taken in which the sides were closed except for a 2-mm opening through which the fringes could be photographed.

The slope of the interference fringe at the plate surface was measured on photographic enlargements which gave a magnification of seven diameters. The heat flux was calculated for different points on the plate from these measurements, using Equation (11).

The curves in Fig. 9 represent the eight cases described above. The solid lines show the heat flux for the four different separations when the sides are closed. The dotted lines show the heat flux when the sides are open. In all cases the heat flux was reduced to the case of a temperature rise of exactly 75 °C above room air. The actual temperature rise differed slightly from this.

Particular note should be taken of the high value of the heat flux near the bottom of the plates. In the case of the plates spaced 0.46 cm apart, the area under the heat-flux curve for the lowest 1.4 cm of the plate is equal to the area under the curve for the remaining 20 cm. The effect is less for a wider spacing of the plates.

The difference between the curves for the sides open and the sides closed can be interpreted as follows. When the sides are open, the column of rising air between the plates draws in cold air from the sides which causes an increase in the average convective heat flux across the upper portion of the plate. On the other hand, when the plates are open at the sides, the velocity of the air between the plates is reduced because of the loss of draught, and the heat flux from the lower portion of the plate is correspondingly less. The effect of closing the sides is to decrease the total convective heat loss by about ten per cent for the 0.46- and 0.69-cm separations, and to increase it by about ten per cent for the 1.13- and the 1.97-cm separations. The actual values are given in Table 1E.

The graphs in Fig. 9 have a direct application to the design of concealed radiators for the heating of buildings. The solid lines should be taken for this study, as the radiator fins are closed at the sides. It is to be noted from these graphs how ineffective in heat transfer is the upper portion of the fin in the usual enclosed radiator.

Table 1. Convective Heat Loss in Watts from the Inner Surface of One of Two Vertical Parallel Heated Plates.

Separation of Plates	0 cm	0.46 cm		0.69 cm		1.13 cm		1.97 cm	
Sides Open or Closed	...	Op.	Cl.	Op.	Cl.	Op.	Cl.	Op.	Cl.
A Power Input Both Surfaces	21.6	26.5	...	30.9	...	34.7	...	37.6	...
B Power Input Inner Surface	0	4.9	...	9.3	...	13.1	...	16.0	...
C Radiation Loss Inner Surface	0	1.0	...	1.4	...	2.2	...	3.2	...
D Inner Surface Convective Heat Loss by Power Input	0	3.9	...	7.9	...	10.9	...	12.8	...
E Inner Surface Convective Heat Loss by Interferometer	...	2.75	2.53	6.32	5.77	8.82	9.84	9.41	10.33
$\frac{D-E}{D}$	...	+0.30	...	+0.20	...	+0.19	...	+0.25	...

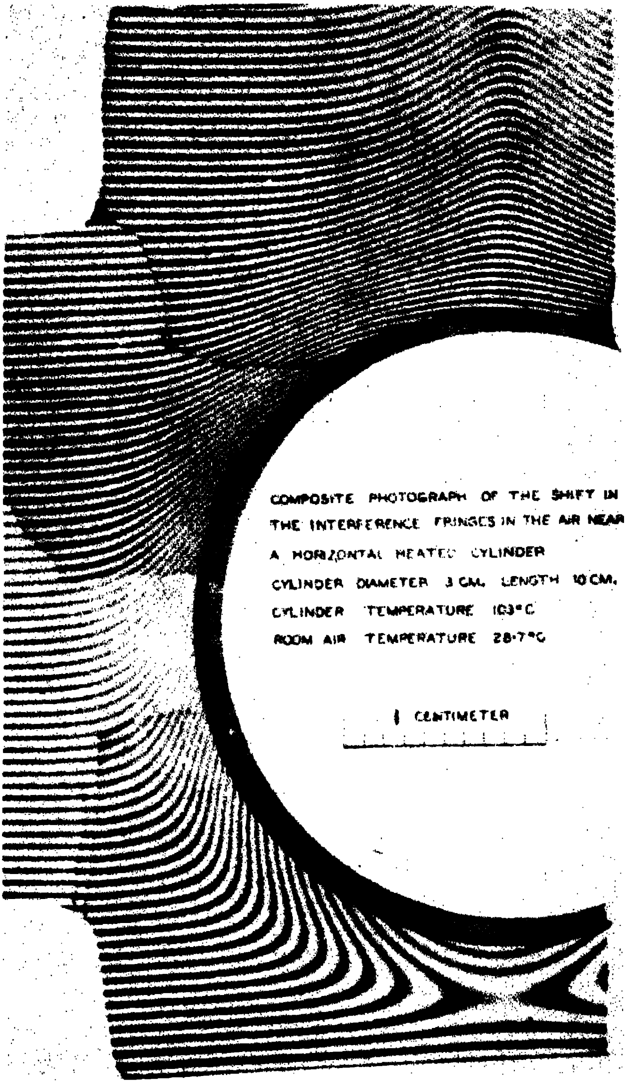

COMPOSITE PHOTOGRAPH OF THE SHIFT IN
THE INTERFERENCE FRINGES IN THE AIR NEAR
A HORIZONTAL HEATED CYLINDER
CYLINDER DIAMETER 3 CM. LENGTH 10 CM.
CYLINDER TEMPERATURE 103°C
ROOM AIR TEMPERATURE 28·7°C
1 CENTIMETER

FIG. 10.
Composite photograph of the fringes about a horizontal heated cylinder 3 cm in diameter.

A comparison was made between the total convective heat transfer as determined by the area under the curves for convective heat flux and that calculated from the power input to the plate, making proper allowance (1) for the power dissipated by the open back and edges of the plate, and (2) by radiation from the inner surface. The heat dissipated by the back and edges was determined by placing the plates in contact, maintaining them both at the same temperature and measuring the power input to one plate. The radiation loss from the inner surface of the plate when separated is a problem combining geometric optics and the Stefan-Boltzmann law of radiation.[24] The inner surfaces were painted with lampblack and blackbody radiation was assumed. As the radiation loss could be determined only for the case when open at the sides, it is only these cases that are compared. These data are tabulated in Table 1.

It is to be noted that the total convective heat loss, as measured by the power input, is from 20 to 30 per cent more than the same quantity as measured by the interferometer. There are several possible reasons for this. In the first place, the heat loss from the inner edges of the plate may be considerably greater when the plates are separated than when they are in contact. In the second place, the heat loss calculated from the interferometer data would be about ten per cent greater if the values for the conductivity of air of Gregory and Archer,[20] were used instead of the more generally accepted values of Eukeh. In the third place, a small amount of very fine-grained turbulence may exist in the air flowing up the plate, which would not exist in the static conditions under which the thermal conductivity is measured. Such turbulence would cause the heat flux to be greater than that indicated by the temperature gradient for pure conduction.

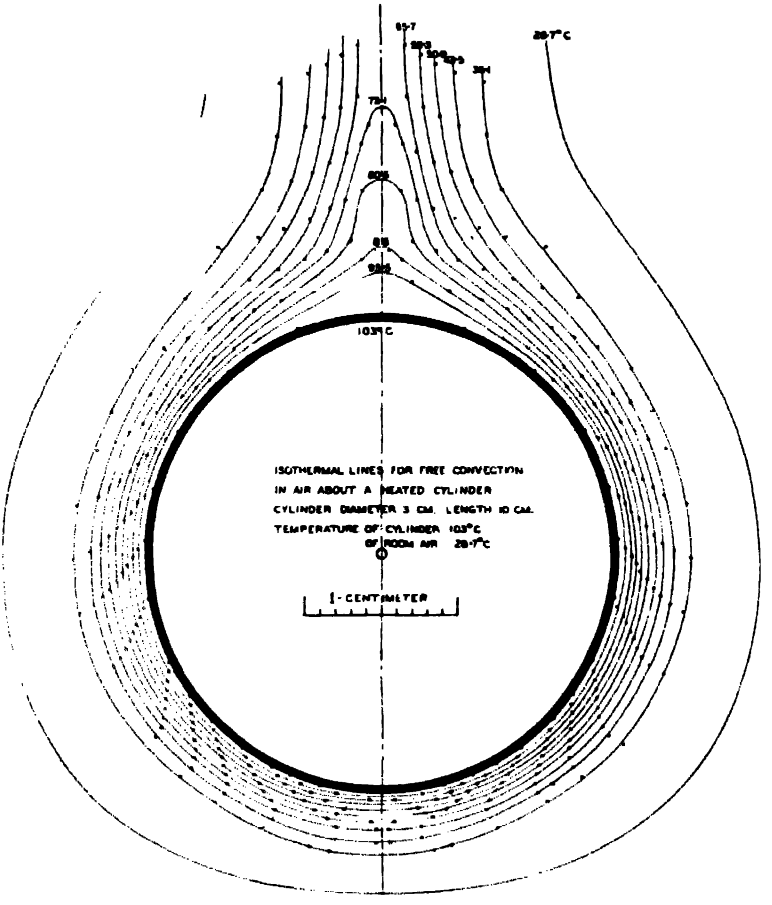
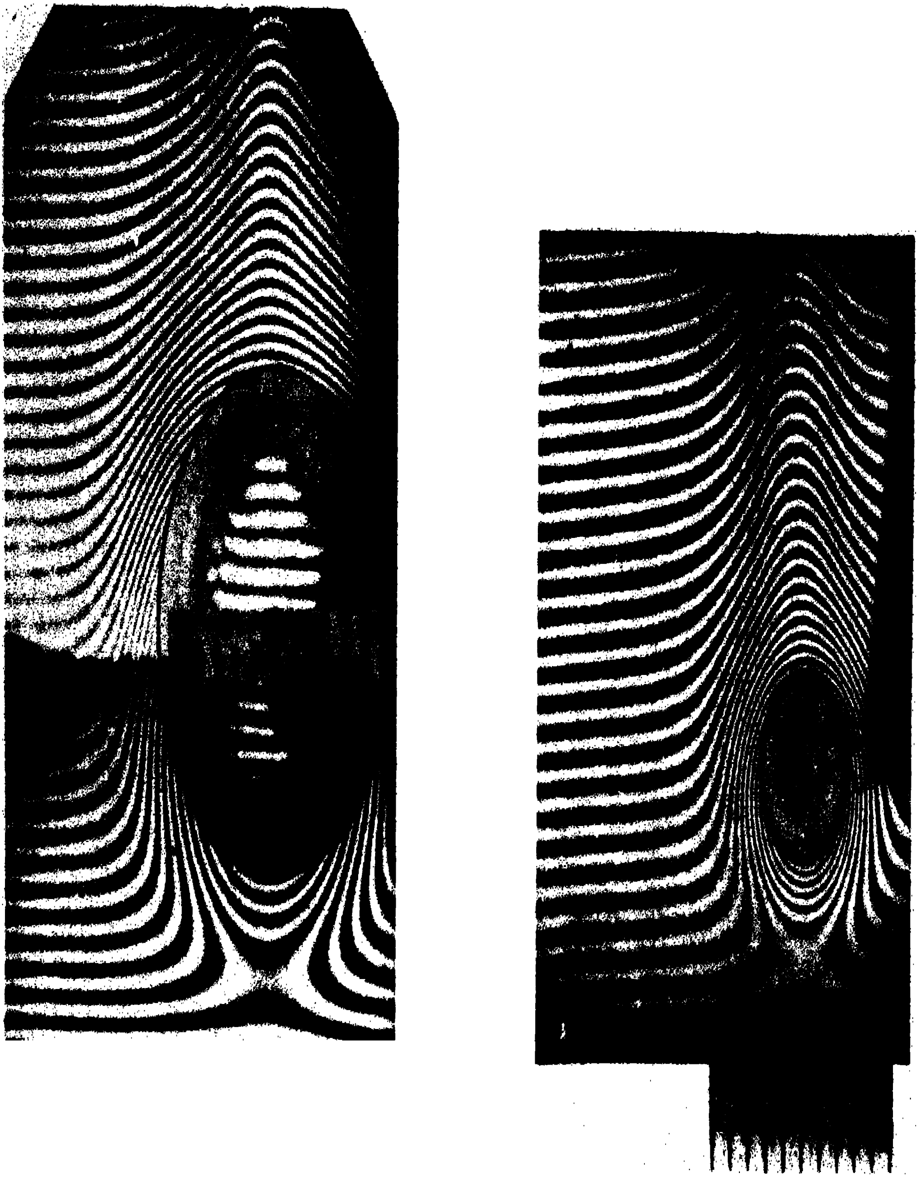

28·7°C
103°C
ISOTHERMAL LINES FOR FREE CONVECTION
IN AIR ABOUT A HEATED CYLINDER
CYLINDER DIAMETER 3 CM. LENGTH 10 CM.
TEMPERATURE OF CYLINDER 103°C
OF ROOM AIR 28·7°C
1-CENTIMETER

FIG. 11. Isothermals about a horizontal heated cylinder.



A. Diameter 1.27 cm

B. Diameter 5 mm

Fig. 12. Fringes about horizontal heated cylinders.

4. Horizontal Cylinders. In Fig. 10 is shown a composite photograph of the fringes about a cylinder 3 cm diameter and 10 cm long. The surface temperature of the cylinder was measured by a thermocouple soldered to the right side of the cylinder, not shown in the photograph. The photographs were taken in the order, upper left, lower left, bottom, and top. The imperfect match between the top and the upper left photograph can be accounted for by a slight shift in the adjustment of the interferometer in the three hours required to complete the set. Such a shift had no effect in plotting the temperature, as the fringe shift in each photograph was measured from the base lines provided by that photograph.

Fig. 11 shows the isothermal lines about this cylinder made by connecting the points of equal fringe shift. The correction for the end effect was made by assuming that the fringe shift at the surface of the cylinder corresponds to air having the temperature of the cylinder, with the appropriate corrections for points at a distance from the surface as previously described. The outer line shows the boundary of the region of heated air. Along this line the temperature is less than 0.3 °C above that of the room. The exact position of this boundary is indefinite, as the fringes show that the departure from room temperature is at first very gradual.

Except for the top of the cylinder, it may be safely assumed that the air flow at the surface of the cylinder is laminar and that the heat flux is proportional to the temperature gradient which may be determined from the spacing of the isothermal lines. If the heat flux at the bottom of the cylinder is taken as 100, it is found to decrease uniformly to 70 at the side. This uniform decrease continues to within 45° from the top, where it begins to drop off more rapidly until the heat flux at the top is only 10. It is not safe to assume that the air flow at the top of the cylinder is laminar. In the case of turbulent air flow, the heat flux would be considerably greater than that indicated by the temperature gradient.

Fig. 12A is a composite photograph of the fringes about a cylinder 1.27 cm diameter and 10 cm long. The cylinder is open at both ends and the interference fringes can be seen through the hollow center. The surface temperature of the cylinder was determined by the thermocouple shown in the lower right of the photograph.

The isothermal lines for this cylinder are shown in Fig. 13A. They were determined in the same manner as for the larger cylinder by connecting points of equal fringe shift. From the spacing of the isothermal lines near the cylinder, the heat flux is found to decrease from 100 at the bottom to 80 at the side to 20 at the top.

Fig. 12B is a photograph of the interference fringes about a cylinder 5 mm diameter. The walls are 1 mm thick and lined with Alundum cement having a 1-mm hole through the center. A straight Nichrome wire serves both as heating element and support. Interference fringes may be seen through the hollow center. As this hole is 100 mm long, the appearance of these fringes gives an idea of the collimation possible with this apparatus.

The isothermals for this cylinder are shown in Fig. 13B. From the spacing of the isothermals the heat flux is found to decrease from 100 at the bottom to 90 at the side to 30 at the top.

The photograph of the fringes about a horizontal platinum wire 0.4 mm diameter are shown in Fig. 14. The current and the potential drop were measured on a potentiometer and the temperature of 101 °C was determined from the resistance. Potential leads were used so that the resistance measured was only that of the straight portion of the wire.

The isothermal lines about this wire are shown in Fig. 15. Only four isothermals have been drawn, as it was not possible to get as many points of equal fringe

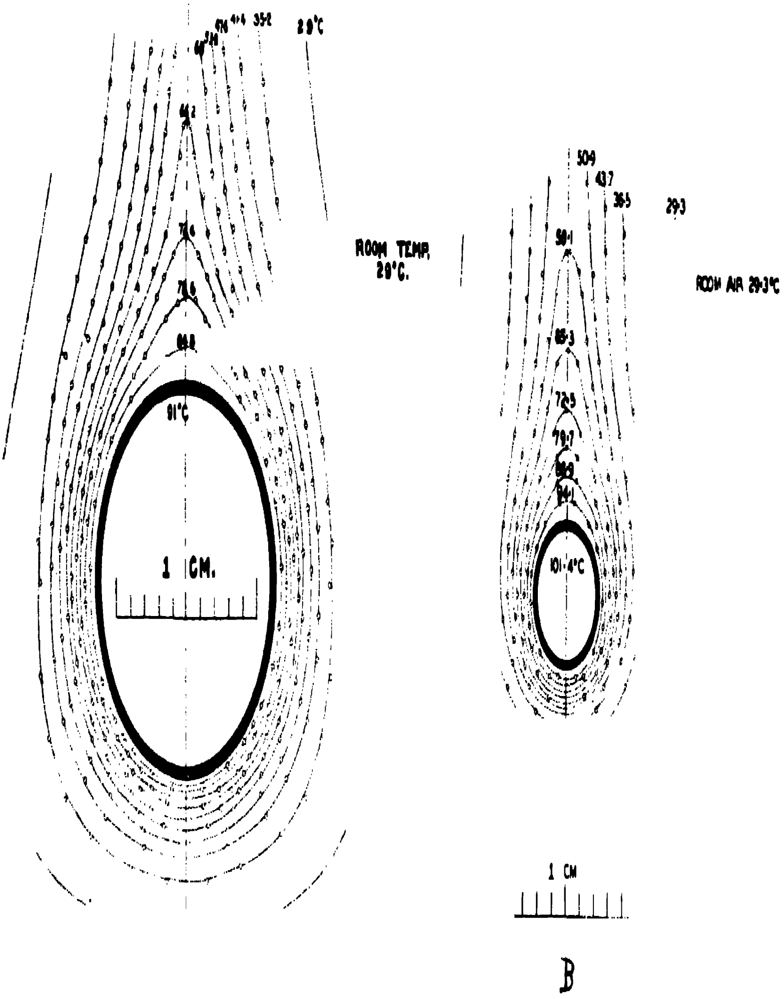


Fig. 13.

Isothermals about horizontal heated cylinders.

A. Diameter 1.27 cm

B. Diameter 5 mm

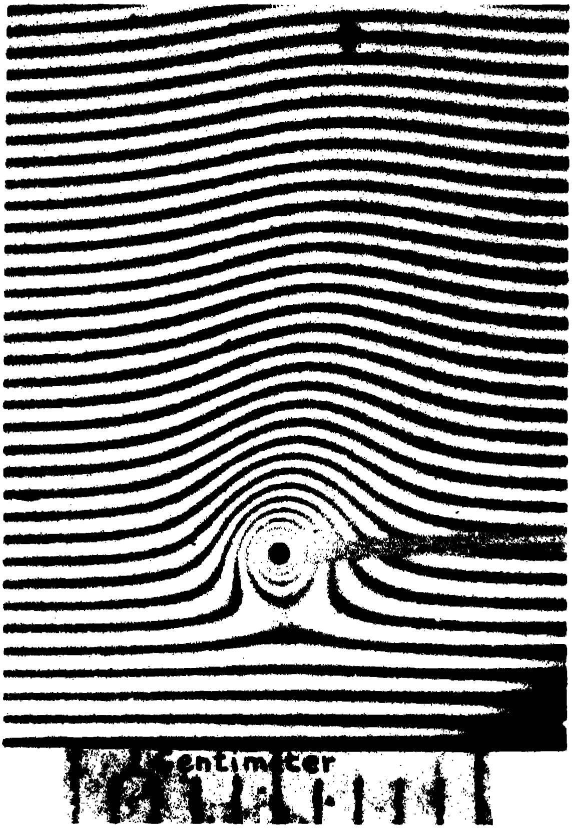


FIG. 14. Fringes about a horizontal heated wire 0.4 mm in diameter.

displacement as in the case of the other cylinders. These isothermals, however, are sufficient to show that the heat flux changes from 100 at the bottom to approximately 90 at the side, to 30 at the top. For the lower portion of this wire the temperature gradient in the air at the surface of the wire is over 700 °C per cm.

In Fig. 16 is given the relative temperature distribution in the air along a horizontal radius out from these four cylinders. The temperature distribution for radial heat conduction from a cylinder may be expressed by the equation

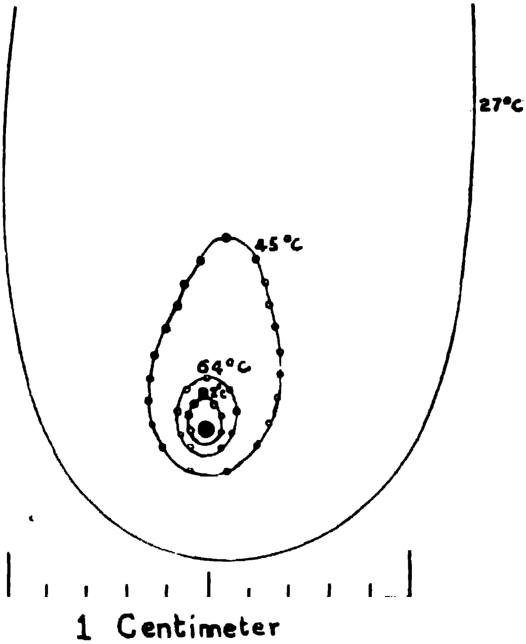
$$t = A - B \log r \tag{16}$$

where t is the temperature and r is the distance from the center of the cylinder. The constants A and B are determined by inserting the values of t and r for two points for which t and r are known, one of which will be the surface of the cylinder. If for the other point we take for t and r the room air temperature and the point along the horizontal radius at which this temperature is first closely approximated, the value for A and B so obtained will give a calculated temperature distribution entirely different from that observed.

If, however, the points chosen are the surface of the cylinder and that for half the temperature drop as determined from the interference fringes, the calculated

Fig. 15.

Isothermals about a horizontal heated wire, 0.4 mm in diameter.



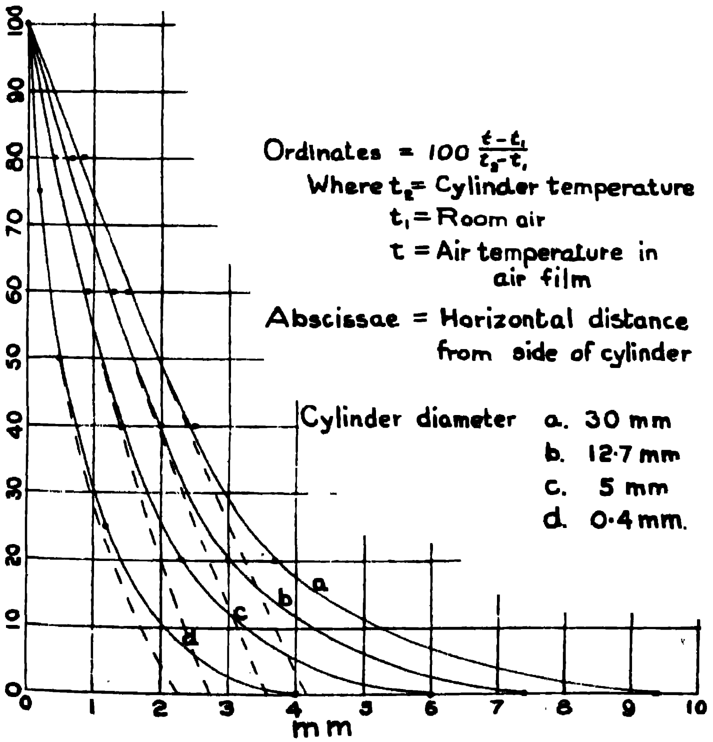


Fig. 16. Comparison of temperature distribution with cylinder diameter.

temperature distribution from the film theory corresponds very closely to that observed from the fringe shifts. The broken lines in Fig. 16 show the temperature distribution when calculated for pure conduction in this manner, and represent the conditions assumed by the film theory. This theory, as developed for cylinders by Rice,[5] also assumes that the temperature distribution would be the same along any radius. Neither of these assumptions is valid. From the isothermal lines about these cylinders it is certain that radial symmetry does not exist. It is also evident that the temperature distribution corresponds to that for pure conduction only for the first half of the temperature drop, and only for the bottom and sides of the cylinder.

As actually used[25] to calculate convective heat transfer, the film theory serves merely as a device whereby experimental results may be correlated by means of dimensional analysis. Experimentally determined coefficients of heat transfer would serve the purpose equally well and not be open to the criticism of being based upon a false physical assumption.

Conclusion

An apparatus has been devised whereby the temperature of the air near heated surfaces may be determined without the use of any material thermometer. This is accomplished by measuring the displacement of the fringes in a suitable interferometer. A series of photographs have been taken of the interference fringes in front of a vertical heated plate, between two vertical heated plates, and about horizontal heated cylinders.

The apparatus also makes it possible to determine the temperature gradient and convective heat flux in the air adjacent to any point on the heated surface. This has not been possible with any apparatus heretofore developed.

Note

The material in this paper on the single vertical plate and on horizontal cylinders is largely drawn from a previous paper by the writer.[26]

The material on vertical parallel plates is published here for the first time.

All the experimental work was done at the Bureau of Standards under the L. B. McMillan Fellowship established from 1930 to 1932 by the Johns-Manville Corporation.

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Flame Temperature

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1. Introduction

In this paper only flames produced incident to the use of fuels for heating and generation of power will be considered. If the fuel is in the gaseous state and is premixed with air or oxygen, after local ignition the burned and unburned gases are separated by a narrow reaction zone or flame front. If the fuel is discharged into the atmosphere, combustion proceeds by interdiffusion of the gaseous or gasified fuel and the air. For organic fuels the latter flames are usually luminous because of formation of soot. This also applies to premixed flames with large excess of fuel.

Other luminous phenomena to which the term *flame* has been applied, such as the cool flames observed in the slow oxidation of gaseous hydrocarbons and in the interdiffusion of alkali metals and halogens, do not warrant discussion here.

2. Theoretical and Experimental Flame Temperature

The quantity *temperature* defines a state of statistical equilibrium and can be assigned only to a system in which such an equilibrium exists. The *theoretical* flame temperature thus corresponds to the following postulated state of complete statistical equilibrium in the burned gas: Collisions between the molecules, and radiation, although continually changing the state of every individual molecule, maintain on the average the randomness of direction of motion and the constancy of (a) the percentage of molecules possessing a given velocity; (b) the percentage of molecules possessing a given quantum state of rotation, of vibration, or of electronic excitation; and (c) the concentrations of dissociation products. The theoretical flame temperature can be calculated[1] for a given content of total energy of the gas from heat capacities and dissociation equilibria obtained by statistical-mechanical methods from band spectroscopic and other data. It is reasonable to assume that in all zones of an actual flame the equilibrium (a) in the translational degrees of freedom is established with close approximation because of the rapidity of the collision sequences; and since for perfect gases, which flame gases resemble, the temperature corresponding to this equilibrium is given by the gas law, an *experimental* flame temperature corresponding to the equilibrium in the translational degrees of freedom may always be obtained by determining the parameters of the gas law, pressure and molar volume. Whether the equilibrium (b) in the internal degrees of freedom and the chemical equilibrium (c) are also established with an approximation sufficient to eliminate measurable differences between theoretical and experimental flame temperatures is to be investigated experimentally.

3. Comparison between Theoretical and Experimental Flame Temperatures in Explosion Experiments

If an explosive gas mixture is ignited at the center of a spherical vessel, the resulting spherical flame does not come into contact with the cold walls of the vessel until combustion is complete, and the theoretical flame temperature can, in general, be calculated without difficult heat-loss corrections. The maximum pressure established at the end of the explosion yields, on the other hand, the experimental flame temperature, the volume remaining constant. Experiments of this type have been carried out extensively for mixtures of hydrogen and oxygen with various inert gases. It was found [1] that with the monatomic gases argon and helium as diluents the experimental and theoretical temperatures are identical within narrow limits of error, but that with diatomic gases like excess oxygen or nitrogen the experimental temperatures are appreciably higher than the theoretical. This indicates that the latter gases are slow to absorb energy in the internal degrees of freedom which they possess in distinction to the monatomic gases, and that equilibrium (b) is not established in the burned gas behind the flame front. The phenomenon has been referred to as excitation lag,[1] implying that the collisional excitation of the internal degrees of freedom, particularly those of vibration, is lagging behind the chemical reaction. Its occurrence suggests caution in the use of molecular infrared radiation from flames for thermometric purposes, particularly if the emitting molecules are introduced into the mixture as diluent gas.

Such excitation lag is also noticeable in experiments with sound waves.[2] A large, rotational excitation lag has recently been reported in the rapid compression of diatomic gases at room temperature [3] and the rapid discharge of steam through an orifice.[4]

4. The Line-reversal Method of Determining Flame Temperatures

a. Theory. The line-reversal method of Féry [5] is based on the assumption that, on introducing certain metal vapors into a flame, statistical equilibrium is established between the electronic degrees of freedom of the metal atoms and the flame gases. The metal atoms thus emit and absorb their spectral lines as thermal radiators.

The quantity measured by the line-reversal method is brightness, B, defined by the equation

$$dE = B\,dA\,dt\,d\omega\cos\theta, \tag{1}$$

where dE is the energy radiated during the time, dt, from an element dA of the surface of a luminous body within the solid angle $d\omega$ at the angle θ to the normal. If the radiation is spectrally unresolved, B is the *total brightness*. If only the energy dE_λ contained in the portion $d\lambda$ of the spectrum (λ being the wave-length) is considered then.

$$dE = B_\lambda\,d\lambda\,dA\,dt\,d\omega\cos\theta. \tag{2}$$

B_λ is called *spectral brightness*. Fundamental optics as well as thermodynamics show that the brightness, B or B_λ, of a body remains constant in the path of any individual light ray emitted by the body regardless of the interposition of lenses or mirrors, provided that the optical system is an ideal one (that is, there is no diffraction or absorption by lenses and mirrors or reflection from lenses) and provided that the medium outside of the optical system is homogeneous and non-absorbing.

The *absorptivity, a*, of any substance is defined as the fraction of incident radiant energy absorbed by it. The *spectral absorptivity, a_λ*, refers to a portion $d\lambda$ of the spectrum as above. A body that has an absorptivity of 1 is known as a blackbody.

The *emissivity*, e, of any substance is defined as the ratio of the brightness of the substance to the brightness of a blackbody at the same temperature. The *spectral emissivity* e_λ is defined correspondingly.

For a thermal radiator of any kind and for any wave-length the relation between emissivity and absorptivity is given by Kirchhoff's law:

$$\frac{B_{\lambda(nb)}}{B_{\lambda(b)}} = e_\lambda = a_\lambda, \tag{3}$$

where nb and b refer to nonblack and black bodies, respectively.

A blackbody obeys Lambert's law; that is, the brightness B or B_λ is independent of θ. It is a function of temperature alone, according to Planck's radiation law:

$$B_{\lambda(b)} = c_1\lambda^{-5}\cdot\frac{1}{e^{c_2/\lambda T}-1}, \tag{4}$$

where $c_1=c^2h=1.40\times10^{-12}$ cal. cm^2 sec^{-1} (c is the velocity of light and h is Planck's constant), and $c_2=\frac{ch}{k}=1.433$ cm deg (k is Boltzmann's constant), and T is expressed in °K.

For short wave-lengths and throughout the visible up to about 0.7μ and for temperatures up to about 3500 °K, $e^{c_2/\lambda T} \gg 1$ and Equation (4) transforms to

$$B_{\lambda(b)} = c_1\lambda^{-5}e^{-c_2/\lambda T} \tag{5}$$

known as Wien's radiation equation.

The line-reversal method rests on the following principle: If a blackbody is placed behind a flame colored, for example, with sodium (which emits the yellow D-doublet, $\lambda=0.5890-6\mu$), and a spectroscope is sighted through the flame onto the blackbody, there will be some temperature of the latter at which its brightness in the spectral region of the D lines equals the brightness of the light transmitted in this region through the flame, plus the brightness of the D lines from the flame itself. At this temperature, therefore, only a continuous spectrum of the blackbody is visible in the spectroscope. At a lower temperature of the blackbody the sodium lines appear bright by contrast against the continuous spectrum. At higher temperatures this contrast reverses itself, the sodium lines appearing dark against the continuous spectrum. At the temperature at which this reversal takes place the following relation applies, if no light is reflected from the flame:

$$B_{D(f)} + B_{D(b)}\,(1 - a_{D(f)}) = B_{D(b)} \tag{6}$$

where the subscript D represents the wave-lengths of the D lines and f refers to the flame. Equation (6) can be transformed to

$$\frac{B_{D(f)}}{B_{D(b)}} = a_{D(f)} \tag{7}$$

This equation is of the form of Kirchhoff's law [Equation (3)]; and if proof can be obtained of the thermal character of the sodium radiation, the temperature of the flame is identical with the reversal temperature.

The metal is usually introduced into the flame as a salt. The salt vaporizes and dissociates into metal atoms and other products. For the measurement of the experimental flame temperature as defined in section 2 it is not necessary for the salt to vaporize completely or for dissociation equilibrium of the salt to be established. It is only necessary that activation and deactivation of the metal atoms by collisions with other molecules be rapid enough to maintain the equilibrium concentrations of atoms in the electronic quantum states involved in the absorption and emission of the spectral line.

b. Experimental technic. Fig. 1 shows a diagrammatic sketch of the line-reversal apparatus as used on stationary flames. The image of a continuous light source (comparison radiator *CR*) is focused onto a portion of the flame above burner *B* by means of lens L_1. Diaphragm *D* defines the beam of light from the flame and comparison radiator, which is brought to a focus on the slit of spectroscope S_p by lens L_2, the composite image completely covering the slit. In practice it is not necessary to use a blackbody as comparison radiator; instead, a light source calibrated against a blackbody in the spectral range under consideration may be used. A convenient comparison radiator is a tungsten band lamp, the brightness of whose central portion can be determined as a function of the electric power input. The calibration can be made with an optical pyrometer which itself has been calibrated against a blackbody. The ordinary optical pyrometer utilizes only red brightness by use of a red filter, $\lambda = 0.665\mu$, but the calibration can be extended to other parts of the tungsten spectrum by using spectral emissivity data[6] and Equations (3) and (5). Other comparison radiators that have been used are a carbon-filament lamp,[5] a Nernst lamp,[7,8] and for very high temperatures a tungsten arc[9] and carbon arc[10] with a rotating sector or absorption glass for diminishing the brightness. If lens L_1 is used between the comparison radiator and the flame, a correction for absorption and reflection due to the lens must be made.[11]

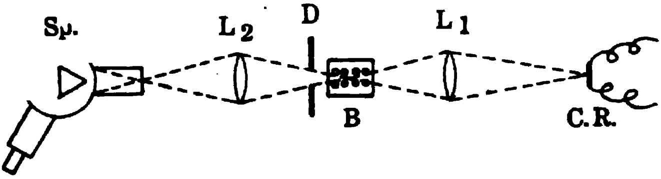

FIG. 1. Diagrammatic sketch of line-reversal apparatus.

The metal may be introduced into the flame[12] either as a spray of a solution of the salt or as a dry dust. The latter may be introduced directly into the flowing gas by mechanical means or by passage of a spark or arc between salt electrodes containing a metal core[13] or between electrodes immersed in powdered salt. In some investigations a piece of salt was placed on the grid of the burner and vaporized by the heat of the flame.[8] The latter method permits coloring of a narrow portion of the flame. It can be accomplished by the spray or dust method if the salt is introduced with a portion of the gas stream passing through a separate smaller tube placed within the burner.

Modifications of the technique of observing the reversal point have been proposed,[12] utilizing the contrast effects afforded by uneven brightness along the observed portion of the tungsten strip.

c. Validity of the Method. There is no instance in the literature in which the gas-law parameters have been determined simultaneously with the line-reversal temperature. Therefore, within the definition of experimental flame temperature (section 2) the line-reversal method has never been tested. With Bunsen burners this could be done in principle by measuring the refraction of the gas stream on passing through the boundary of the inner cone, using the relationship[14]

$$\frac{\rho_u}{\rho_b} = \frac{\tan\beta}{\tan\alpha'} \tag{8}$$

where ρ_u and ρ_b are the densities of the unburned and burned gases, respectively, α the angle at which the gas stream enters and β the angle at which it leaves the reaction zone. Accurate measurements of β are very difficult.

There is, however, a wealth of other material that has established the validity of the line-reversal method. Using a large Méker burner and coal gas-air mixtures, Bauer[7] found identical reversal temperatures with a number of different

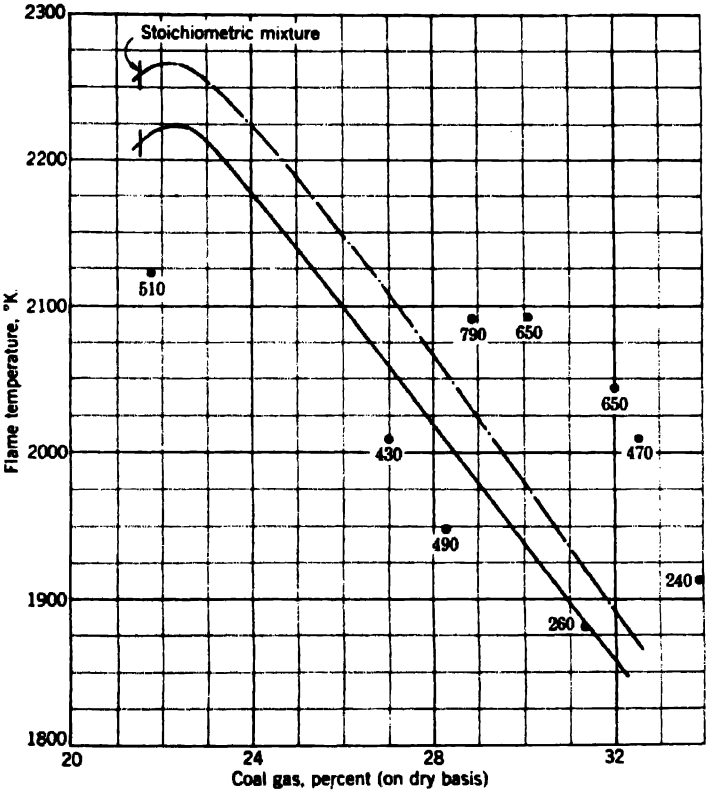

FIG. 2. Comparison of theoretical flame temperatures of coal gas-air mixtures with experimental flame temperatures determined by the line reversal method.

—·—·— Theoretical curve, dry mixtures.

— — — Theoretical curve, moist mixtures.

● Sodium line-reversal flame temperatures with gas velocity in centimeters per second.

salts of sodium and salts of other metals with characteristic line emissions in all parts of the visible spectrum. It does not seem possible to interpret this result in any other way than that statistical equilibrium is established in all cases, either completely or at least between the electronic degrees of freedom of the metal atoms and the translational degrees of freedom of the gas. Since the mixture compositions were not known well enough to allow a comparison between the theoretical calculated temperatures and the reversal temperatures, no estimate can be made of the extent to which equilibrium was attained in these experiments. Kohn[8] confirmed Bauer's result of the reversal temperature on the nature of the salt, using again a Méker burner and coal gas-air mixtures of unknown composition. Furthermore, Kohn compared the reversal temperature with the temperature of a wire immersed in the flame and compensated electrically for radiation, using a procedure described by Schmidt.[15] A wire inserted in a flame emits radiation in a continuous spectrum for which the flame is essentially transparent; it reaches a temperature lower than that of the gas, at which the flow of energy from the gas to the wire equals the energy radiated from the wire. The wire is now heated by an electric current to a temperature at which there is no further flow of energy from the gas to the wire. The exact amount of current can be determined from knowledge of the radiated energy per unit length of wire as a function of the wire temperature and increasing the wire temperature in the flame until the electric power input equals the radiant energy. The temperature so determined was found to be identical with the line-reversal temperature measured in the neighborhood of the wire. Thus, the same equilibrium exists between the gas and the solid metal as between the gas and the vaporized metal atoms.

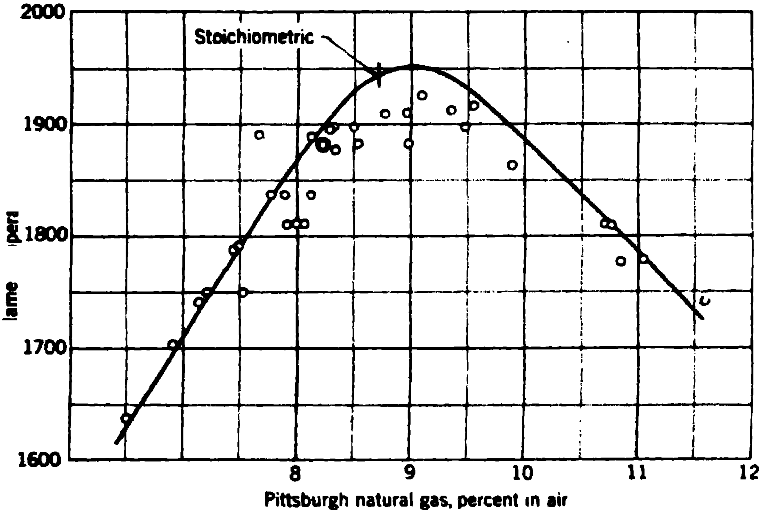

FIG. 3. Highest flame temperatures of Pittsburgh natural gas-air mixtures observed in center of Méker burner flame by sodium line-reversal method.

Calculation of theoretical flame temperatures for known mixtures is complicated by heat losses to the burner grid and also to the surroundings by radiation and intermixing. In the case of excess fuel, secondary combustion occurs in the outer parts of the flame. There exists, however, a zone of considerable height and width above the grid in which the temperature is quite uniform and in which, therefore, the disturbance due to contact with the atmosphere is negligible, and only losses to the grid and by radiation are important. Reversal temperatures in this zone of Méker flames of known coal gas-air composition and varying flow velocities of the gas were determined by Minkowski, Müller and Weber-Schäfer.[16] Comparison of their values with the theoretical flame temperatures calculated for adiabatic combustion shows that for high enough flow velocity the reversal temperature exceeds the theoretical temperature (see Fig. 2).* In view of Bauer's and Kohn's results establishing the validity of the line-reversal method, this indicates the existence of excitation lag in the flame gas similar to that found in explosion experiments described in section 3. Fig. 2 also shows that the gas velocity required for the reversal temperature to transcend the theoretical temperature becomes larger toward stoichiometric mixtures. This is believed to be, in part, a consequence of the higher burning-velocity of mixtures nearer the stoichiometric, because the higher the burning-velocity the closer the flame burns to the grid for a given flow-velocity, and the greater the heat loss. Part of the effect must also be attributed to the higher flame temperatures of such mixtures, causing more rapid heat transfer.

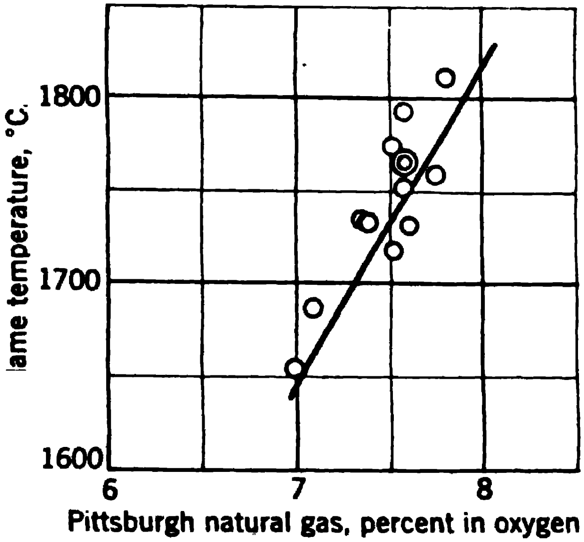

FIG. 4. Highest flame temperatures of Pittsburgh natural gas-oxygen mixtures observed in center of Mêker burner flame by sodium line-reversal method.

' Theoretical flame temperatures.
O Observed flame temperatures.

Reversal-temperature measurements by Kaveler and Lewis[13] on slow-burning natural gas-air flames agree very closely with the theoretical temperatures for adiabatic combustion (Fig. 3). Only in the neighborhood of the stoichiometric mixture do the reversal temperatures fall somewhat below the theoretical curve, which may be explained in the same way, namely, greater heat loss to the grid for higher burning velocities. If oxygen is substituted for the atmospheric nitrogen in lean mixtures the reversal temperatures are on the average somewhat above the theoretical curve (Fig. 4), which is another indication of excitation lag, it being known from explosion experiments that this effect is considerably larger for oxygen than for nitrogen.

In all the investigations mentioned the experimenters were careful to color only the portion of the flame being investigated. If the entire flame is colored the

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* Two limiting curves for dry and saturated gases were calculated since the water vapor content was not known.

reversal temperature should lie between values for the gas at the center and the gas at the boundary. The latter is cooler than the former in lean mixtures, and hotter, owing to secondary combustion, in rich mixtures. Some early work of Kurlbaum and Schulze,[17] which seemed to indicate dependence on the nature of the salt, was shown by Bauer [7] to be in error owing to the use of totally colored flames.

In flames of organic fuels the reaction zone is colored blue or green (Swann bands) depending on the mixture composition. This emission is due to C—H or C—C (Swann bands) radicals, respectively. Since these radicals are formed as intermediates in the combustion reaction and probably are excited in the act of formation, it might be expected that their electronic quantum states are not in statistical equilibrium. This is confirmed by observations of Bauer,[7] who applied a modified line-reversal method to these bands and obtained temperatures, obviously fictitious, which were many hundreds of degrees higher than the possible maximum temperature of the flame. This result has been confirmed independently by Tawde and Patel.[18]

5. Determination of Flame Temperature by Wires and Thermocouples

If a wire or thermocouple is inserted in a flame for thermometric purposes allowance must be made for the temperature difference between wire and gas due to radiation (see section 4c). This may be done in two ways: (1) by using a series of progressively thinner wires and extrapolating the measured wire temperatures to zero thickness; (2) by compensating the radiation by means of electrical heating. The latter method requires determination of the energy radiated from the wire per unit length and time as a function of its temperature. This may be done either by measuring the radiation with a thermopile for a series of pyrometrically determined wire temperatures [15] (these measurements may be performed with the wire in any transparent medium, such as the open atmosphere *) or by measuring the electric power input for a series of pyrometrically determined temperatures with the wire placed in a high vacuum so that conduction and convection losses are eliminated.[9]

In the various suction pyrometers [19] used in furnace work the thermocouple is enclosed in a tube through which the furnace gas is passed rapidly enough to bring the walls of the tube to the temperature of the gas. There is thus no radiation loss from the thermocouple to the colder furnace walls. Sometimes the walls of the tube are heated electrically, with the current so adjusted that the thermocouple reading remains the same whether the gas is flowing or not.

6. Determination of Flame Temperature by Measuring Brightness and Absorptivity in the Infrared

The temperature of a thermal radiator can be determined by direct measurement of its brightness and absorptivity in some spectral range. The relation between these quantities is given by Equations (3) and (4). Such measurements were made by Schmidt [18] for wave-lengths between 2.7 μ and 4.4 μ (bands of H_2O and CO_2) and by Bauer [7] for wave-lengths in the region of 25 μ (residual rays of fluorite). Both investigators used large Méker burners and coal gas-air mixtures. Schmidt also measured the temperature of the flame by a wire in the manner described above and found fairly good agreement between the temperatures obtained by both methods. Bauer found similar agreement between his measured infrared temperature and the line-reversal temperature. It is not easy to appreciate the significance of these experiments because infrared absorption and emission take place throughout the entire depth of the flame on which the instrument is sighted and it is not possible to single out a narrow zone, as in the line-reversal and wire methods. Thus, the temperature obtained by the infrared method should be intermediate between extreme values existing in the flame, as would be the case with the line-reversal method if totally colored flames were used.

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* Convection and conduction losses do not affect these measurements as has sometimes been erroneously supposed.

7. Measurement of Temperature and Emissivity of Soot-forming Luminous Flames

The slowness of the combustion process in soot-forming, luminous flames of the pre-mixed type with rich mixtures, or of the diffusion type, insures the absence of any appreciable excitation lag effect, particularly in view of the experience of Kaveler and Lewis [18] with natural gas-air mixtures burning relatively much faster. Thus, the luminous flame has a temperature corresponding to the definition of the theoretical flame temperature—it is a thermal radiator, the bulk of the radiation being emitted by the soot particles as a continuous spectrum. The soot particles, being cooled by radiation more strongly than the surrounding gas, are at a somewhat lower temperature than the latter. On the basis of data on particle size and heat transfer of solid bodies in gaseous media, Schack [20] has estimated that the temperature difference between the soot particles and the gas should be substantially less than 1 °C at usual flame temperatures.

For measuring the temperature of a luminous but not opaque flame Kurlbaum [21] proposed a method similar to the line-reversal method. An optical pyrometer is sighted on a blackbody with and without the flame between them. The temperature of the blackbody is adjusted until its brightness, as seen through the pyrometer, is the same as that observed with the flame interposed. Equation (6) applies, which means that both flame and blackbody are at the same temperature given by the pyrometer reading. Other comparison radiators may be substituted for the blackbody. This method is not easily applicable to industrial furnaces.

Since the presence of soot particles greatly increases the heat transfer by radiation in furnaces, much thought has been given to the determination of emissivity of luminous flames from temperature measurements. Schack,[20] after reviewing the data on light absorption of soots from various sources, came to the conclusion that the spectral absorptivity of the flame can be represented by the absorption law for homogeneous absorbing media, namely

$$a_\lambda = 1 - e^{-k_\lambda L} (= e_\lambda, \text{ see equation 3}), \tag{9}$$

where L is the thickness of the absorbing layer and k_λ is the absorption coefficient which, over a limited range of wave-lengths, can be represented by the equation

$$k_\lambda = \frac{k}{\lambda^\alpha}, \tag{10}$$

where k and α are constants. Introducing the spectral *brightness temperature, T_λ* of the flame, which is the temperature of a blackbody of equal spectral brightness, one obtains from Equations (3) and (5)

$$\frac{1}{T} - \frac{1}{T_\lambda} = \frac{\lambda}{C_2} \ln e_\lambda \tag{11}$$

where T is the true temperature of the flame. If T_λ is measured for a given wave-length and T is determined independently, the absorption strength, $k_\lambda L$ may be calculated from Equations (9) and (11), and since values of α are known over the entire spectral range, e_λ is also known as a function of the wave-length. The desired quantity—the total emissivity of the flame—can then be calculated from Kirchhoff's law for total brightness,

$$\frac{\int_0^\infty e_\lambda B_{\lambda(b)} d\lambda}{\int_0^\infty B_{\lambda(b)} d\lambda}, \tag{12}$$

$B_{\lambda(b)}$ being given as a function of λ by the Planck Equation (4).

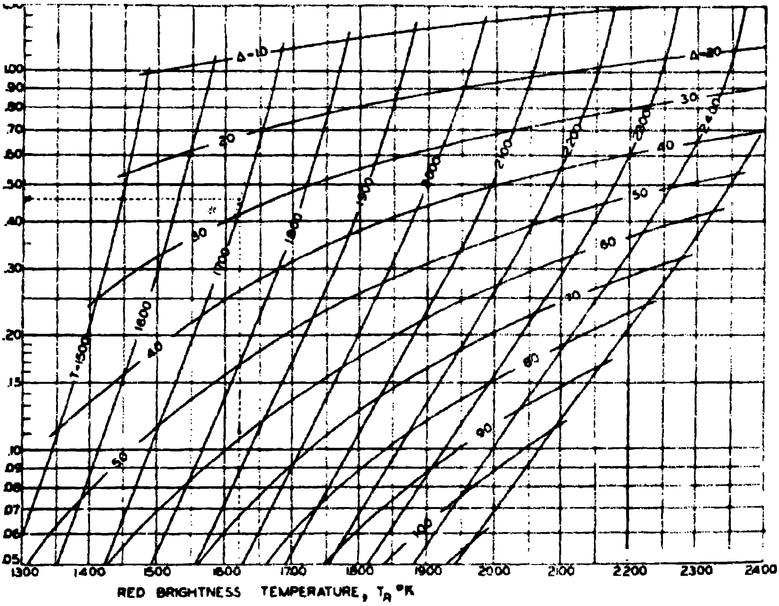

FIG. 5. True temperature and absorption strength of luminous flames, as functions of red and green brightness temperatures (Hottel and Broughton).

Schack suggested measuring the brightness with an optical pyrometer and the true temperature by some other method, such as a suction thermometer. But, as he himself pointed out, the latter method does not allow precise determination of the usually small difference between T_λ and T, mainly because of the use of two entirely different types of instruments. Hottel and Broughton[22] overcame this difficulty by employing the optical pyrometer exclusively and determining T_λ in two spectral regions, the red and green. Two equations of the type of (11) may now be written with $T_\lambda = T_{\text{Red}}$ and T_{Green}. Hence, T can be eliminated; otherwise the procedure for calculating e remains as before. Hottel and Broughton made further studies of the best values of α to be used. They are $\alpha = 1.39$ up to $\lambda = 0.8\,\mu$ and $\alpha = 0.95$ from $\lambda = 0.8\,\mu$ to $10\,\mu$. To eliminate tedious calculations, Hottel and Broughton constructed the following two graphs from which the true temperature and total emissivity may be read, knowing T_R and T_G. From the value of T_R on the abscissa of Fig. 5, one goes vertically to the proper value of $(T_G - T_R)$, then reads the true temperature, T, by interpolation on the semi-

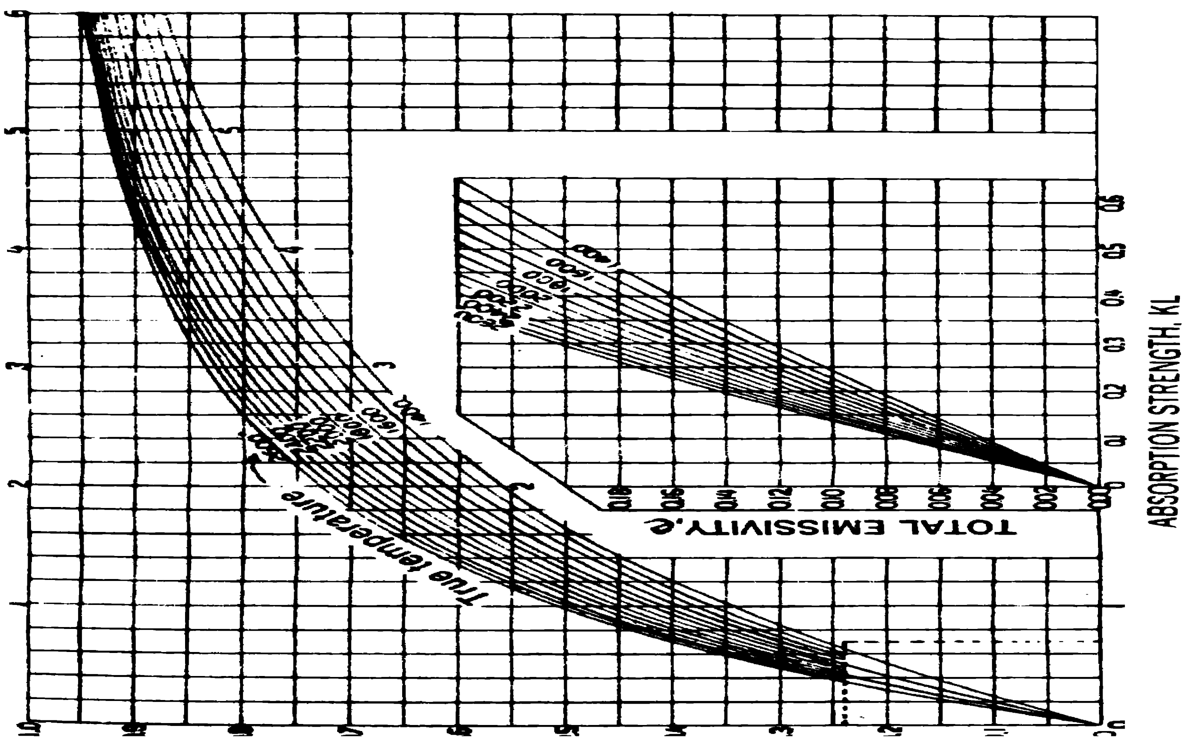

FIG. 6.

Total emissivity of luminous flame from its true temperature and absorption strength (Hottel and Broughton).

vertical lines and *kL* on the ordinate. With this value of *kL*, *e* is read from Fig. 6 for any true flame temperature.

Another method adapted to industrial work, namely color pyrometry,[23] makes use of the fact that for many nonblack radiators (so-called gray bodies) the ratio of the spectral brightness for two wave-lengths is about the same as for a blackbody. In its simplest form, the color pyrometer consists of a bichromatic, wedge-shaped light filter that transmits only red and green. The coefficients of extinction of the two colors differ; as the thickness of the wedge is increased green is absorbed more completely than red. When a radiating body is observed through this type of filter it appears green when viewed through the thin end and red through the thick end. At a certain point in the wedge these two colors, being complementary, merge into white. The position of this point in the wedge depends on the ratio of the red and green brightnesses of the radiating body, *i.e.*, on its temperature, and the length of the wedge can thus be calibrated in terms of temperature. Other, more elaborate instruments have been designed with compensating devices for nongray bodies and for overcoming physiological errors.

8. Concluding Remarks

Experimental flame temperatures significantly higher than theoretical temperatures have been observed only in fast flames such as hydrogen and coal-gas flames. In furnace flames there appears to be no reason to expect appreciable deviations from statistical equilibrium except perhaps near the orifice in premixed flames—disturbances such as heat transfer are too slow to affect the statistical equilibrium. Thus, there is no anomaly to be dealt with and temperature measurements should give the true flame temperature that corresponds to the theoretical flame temperature as defined in section 2.

In internal combustion engines where the flame is greatly speeded up by turbulence, appreciable excitation lag may occur, but owing to the complexity of the process there seems to be no practical way at present to determine its contribution to the pressures developed. Rassweiler and Withrow[24] determined a temperature of 2060 °C at the firing end of an Otto cycle engine, using the line-reversal method. This temperature was calculated later by Hottel and Eberhardt[25] to be 2071 °C on the basis of adiabatic combustion. The measured temperature is undoubtedly lowered by cooler gas layers near the observation window.

The flame temperatures of various combustibles and the change of flame temperature with the air-fuel ratio can be compared from calculations on the basis of adiabatic combustion. These calculations are tedious and have been done with accurate data only for a few cases.[1] In most instances where less accurate, older data have been used, the results are in error by not more than 50° and may still be used as a basis of comparison of various mixtures. Lacking calculated values, the large amount of data of line-reversal temperatures may prove useful, although these data were, as a rule, obtained with totally colored flames. Such line-reversal temperatures are uniformly lower than the theoretical temperatures by amounts ranging from 30 to 80 °C. Extensive tables have been compiled by Lewis and von Elbe.[26]

In gases where the statistical equilibrium is very strongly disturbed, such as in discharge tubes and in the hydrogen torch the term *temperature* loses much of its practical significance, although it may still be a definable quantity on the basis of the translational energy of the gas. Pirani and Rompe[27] have proposed to denote the degree of freedom or the molecular state that primarily acquires the energy added to the system as "energy flow trap." For ordinary flame gases this term does not seem to be usefully applicable.

Summary

The discussion is confined to flames that are produced in the use of fuels for heating and generation of power. The theoretical flame temperature corresponding to complete statistical equilibrium in the burned gas is distinguished from the experimental flame temperature measured by the gas-law equation and corresponding to equilibrium in the translational degrees of freedom. Experiments on fast flames in closed vessels show that the latter may be higher than the former due to excitation lag in the internal, presumably vibrational, degrees of freedom.

The theory and technic of the line-reversal method are described, and the experimental evidence is interpreted as indicating that the method yields the experimental flame temperature as defined above. The technic of measuring flame temperatures by wires and thermocouples is described. In measurements of flame temperatures by infrared radiation temperature variation within the flame is a disturbing factor.

Soot-forming luminous flames may be regarded to be in complete statistical equilibrium, the temperature difference between soot particles and the surrounding gas being negligible. Methods of determining the temperature and emissivity of such flames are described. In industrial furnaces the differences between the experimental and theoretical temperatures should be negligible, and there is thus no reason to question the existence of a true temperature. In internal combustion engines excitation lag is likely to exist, but no experimental confirmation is available. The term "energy flow trap" does not seem to have useful application in technical combustion processes.

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High-Temperature Gas Measurements in Arcs

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Introduction

In recent years a good deal of effort has been devoted to the problem of measuring the temperatures in the discharge column of the arc. Because these temperatures are generally high compared to those found in laboratory or industrial furnaces, the means of measurement have developed along unusual lines which may have application in other fields. With that possibility in mind, measurement principles, technics, and some of the results which have proved useful in arc studies are herewith described.

It has been known for a long time that the temperature of the gas in the core of the arc is sufficiently high to melt, sublime, or decompose all known substances. This fact has been an impediment to the use of methods of gas thermometry which are satisfactory at somewhat lower temperatures.

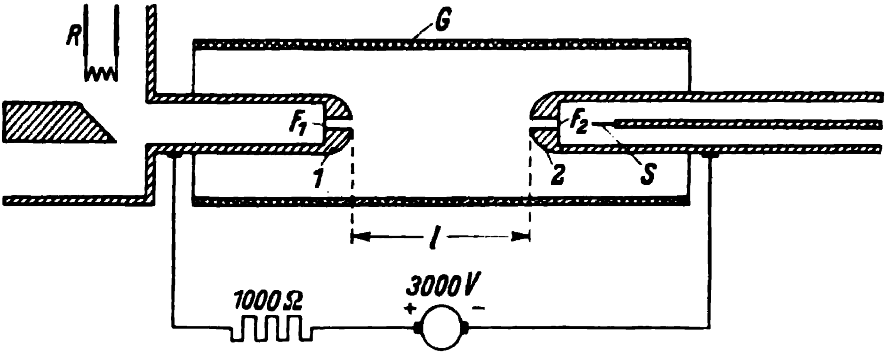

Fig 1. Arc electrodes arranged for gas density measurement by x-ray absorption (von Engel and Steenbeck). *R*, x-ray tube; F_1, F_2, .28 × 10^{-3}-inch aluminum windows; ionization counter electrode; *G*, stabilizing tube.

Gas Temperature from Density Measurements

A simple physical fact upon which the measurement of gas temperature can be based is the temperature dependence of density. The gas density varies as $1/T$ °K in a monatomic gas, or in a polyatomic gas below the temperatures of decomposition or dissociation. This potentially simple method of temperature measurement has been developed by von Engel and Steenbeck[1] and by Ramsauer,[2] who have used x-ray absorption, α-particle, and electron absorption for measuring the gas density. A somewhat similar x-ray method was used earlier by Dauvillier[3] in glow discharges. To measure gas temperature by this method it is not sufficient experimentally to determine the density; but, in common with all methods which have been used at the highest temperatures, a good deal must be known also about the nature of the gas. For example, in a mixture of polyatomic gases, the partial pressure and constitution of each of the dissociation products must be known over the measured range of temperature. Since this information is also required for the velocity of sound method described subsequently, a detailed discussion of the question will be deferred to that section.

Methods of Measuring Gas Density. The arrangement of the x-ray source and receiver for von Engel and Steenbeck's method is shown in Fig. 1. The x-ray aperture, in the form of a water-cooled electrode, 1, employs a 7 μ aluminum window of 2-mm aperture. This window is as near the high-temperature gas as possible (about 0.8 cm) to minimize end effects, since the absorption over the intervening cool path is relatively important.

At the receiving end the x-ray intensity is measured with a Geiger counter similarly enclosed in a water-cooled electrode and protected by an aluminum foil window. The end corrections are made by observing the absorption over gas paths of various lengths, whereby the end correction can be eliminated as a difference. The end correction is so large, however, that relatively great accuracy in the measurement of total absorption is required if the heated path is short and the temperature high. For example, in air, let the density $\rho = 1$ at an absolute temperature of 300 °K. At 3000 °K, $\rho = 0.1$, while at 6000 °K, $\rho = 0.03$, the decrease beyond that calculated from $1/T$ being due to dissociation. If the temperature varies linearly from 300 to 3000 °K over two paths of total length 1.6 cm, the average density will be 0.65. A path of 1.6 cm of constant density 0.65 will absorb as much as 10.4 cm of gas at 3000 °K. For measurement means of similar geometry in a gas at 6000 °K and under similar assumptions, the 1.6-cm end path will absorb as strongly as 21.3 cm of hot gas. It is clear that density measurements over very short paths of high-temperature gases will be subject to large errors due to end corrections; and, conversely, when the path may be long, as in a furnace, relatively high accuracy can be expected.

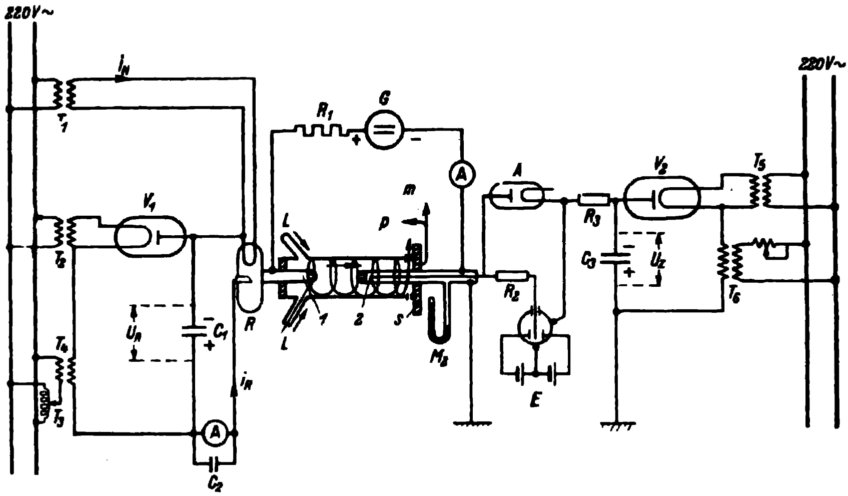

Fig. 2. Complete circuit diagram for x-ray density measurement. V_1, T_4, high-voltage source for x-ray tube R; E, electrometer for ionization counter.

The absorption of a parallel x-ray beam is given by a relation of the form

$$I = I_0 e^{-a\rho l},$$

where I_0 is the emission intensity, I the intensity at a distance l through a path of uniform density ρ and absorption coefficient α. The system may therefore be calibrated over a shorter path at room temperature, or a longer path at room temperature and reduced pressure. The complete circuit for the x-ray source and the Geiger counter is shown in Fig. 2, which is taken from von Engel and Steenbeck. The high-voltage rectifier tube, V_1, the x-ray tube, R, and associated apparatus comprise the radiation source; and the Geiger counter ionization meter employs the ionization chamber, 2, and electrometer, E, as an output device.

In subsequent work[4] these authors used α-particles from polonium as the radiation source as an alternative to a beam of x-rays. This eliminated fluctuations in the beam due to line voltage variations and, in addition, provided an absorption curve which greatly minimized the end zone corrections.

As an alternative to either of these sources, one may employ the electron beam from a Lenard tube, as in Ramsauer's[2] method. All the information available about this method, however, appears in a brief report of work in progress in the A.E.G. laboratory by G. Dobke. In the absence of a subsequent detailed publication, the advantages or disadvantages of the method are not known.

Temperature Measurement by Sound Velocity

It was suggested by Mayer[5] in 1873 that the velocity of a sound wave might be used to measure gas temperatures. The special advantages of the method for high-temperature gases were explored by Anderson and Smith,[6] who reflected sound waves from exploding wires back into the discharge for measuring the temperature of the metal vapor. Extensive use of the method has since been made in arc studies[7a,b,c,d] where two means of using the principle have been developed.

Theoretical Considerations. The velocity of propagation, c, of small disturbances through an elastic medium is given by the well-known relation

$$c^2 = \frac{dp}{d\rho}, \tag{1}$$

where p and ρ are, respectively, the pressure and density of the medium. It was discovered very early by comparing measured and calculated velocities that the transient pressure changes involved in the transmission of sound in air are adiabatic. For the adiabatic case, and replacing ρ by M/V, where M is the molecular weight and V the volume of a gram molecule, (1) becomes

$$c^2 = -v^2/M \frac{1 + (\rho/C_v)(\partial v/\partial T)_p}{(\partial v/\partial p)_T} = -(v^2/M)(\partial p/\partial v)_T\gamma, \tag{2}$$

where $\gamma = C_p/C_v$, and C_v, C_p are the specific heats in ergs per gram molecule. It may be shown[7c] that when the elastic medium is a mixture of non-reactive gases which individually and as a mixture obey the perfect gas laws, (2) reduces to

$$c^2 = \left(\frac{RT}{M}\right)\left(1 + \frac{R}{C_v}\right). \tag{3}$$

In (3) M and C_v are the weighted mean molecular weight and specific heat where the weight may be taken equal to the partial pressures, p_i, of the gaseous components; thus

$$M = \frac{\Sigma p_i M_i}{\Sigma p_i} \tag{4}$$

$$C_v = \frac{\Sigma p_i C_{vi}}{\Sigma p}. \tag{5}$$

Both M and C_v are, of course, functions of the temperature. R is the gas constant $= 8.316 \times 10^7$ erg deg^{-1}, and T is the absolute temperature.

It is thus necessary to have specific heat and dissociation data for all the components of the gas, if it consists of a mixture, over the measured range of temperature. This information is now available for many gases at high temperature,[8] so that the curve of sound velocity as a function of temperature can be calculated.

In the general case the NO equilibrium

$$\mathrm{NO} \rightleftarrows \tfrac{1}{2}\,\mathrm{O_2} + \tfrac{1}{2}\,\mathrm{N_2} + .9\ ev$$

must be taken into account when all contributions to the specific heat of air are considered. However NO is stable relative to O_2 and N_2, but not relative to N and O. Hence the NO formation becomes small in the range above 3000 °K. Below 3000 °K the NO reaction will contribute to the specific heat, but since the dissociation energy is small, the effect on the sound velocity is negligible for most purposes. It may be added that the NO bands are never seen in the spectra of arcs in air at atmospheric pressure.

The available specific heat tables for polyatomic molecules, which in some cases extend to 5000 °K, include the contribution due to rotational and vibrational energy levels obtained from spectroscopic data and are of a high order of accuracy. Even at temperatures as high as 5000 °K the contribution of excitation levels to specific heat is negligible, so that for the monatomic dissociation products there is no reason to doubt that the classical $C_v = 3/2\,R$ is valid. The conversion of the C_p data for polyatomic molecules to C_v must, of course, be made by the relation $C_p = C_v + R$ and not as $C_p = \gamma C_v$.

As an illustration of an application of specific heat and dissociation data to this problem, the case of high-temperature sound velocity in air is cited. In Table 1 are given the equilibrium constants,

$$k_1 = p_{\mathrm{N}}^2/p_{\mathrm{N_2}} \qquad k_2 = p_{\mathrm{O}}^2/p_{\mathrm{O_2}},$$

the weighted mean specific heats, the weighted mean molecular weight, and finally, the velocity of sound for temperatures up to 5000 °K. Whereas the velocity of sound varies as $T^{1/2}$ in a perfect monatomic gas, the variation in air in the range 3000-5000 °K is more nearly proportional to T as a result of the high-temperature dissociation.

Table 1. Sound Data for Air.

T °K	k_1	k_2	C_v	M	c(cm sec^{-1})
3000	3×10^{-7}	1.42×10^{-2}	6.76	28.15	1.072×10^5
3500	2×10^{-5}	0.268	6.24	26.32	1.207
4000	7×10^{-4}	2.45	5.76	24.44	1.35
4500	1×10^{-2}	13.8	5.31	23.10	1.50
5000	8×10^{-2}	55.4	4.97	21.57	1.64

In the general case the possibility that the vibrational and rotational equilibria are not fully established during the period of the sound passage and hence that dispersion phenomena exist must be considered.[9] To demonstrate this dispersion, however, it has been necessary to perform experiments at supersonic frequencies and then generally with specific molecules such as CO_2. In the case of air, for example, sound velocities calculated from specific heats which include a substantial contribution from diatomic degrees of freedom are in excellent agreement with measured values, even at supersonic frequencies. By using pressure pulses, which have most of their energy in the equivalent low-frequency spectrum, the possibility of vibrational-rotational dispersion in any case becomes very remote. The case of dissociation dispersion is considered next.

Velocity Dispersion from Dissociation Lag. In the treatment given above the sound velocity in a gas is determined on the basis of a $\bar{C}_v$ which does not depend upon the frequency of the sound wave.

In what follows we shall refer to the "frequency" of a sound wave although the experimental methods have developed around a pressure pulse or single wave front. For the present purpose it will not be necessary to examine this difference in detail, since in treating dispersion phenomena we will have occasion to refer only to the infinite frequency and zero frequency velocities c_∞ and c_0.

In the general case, however, $\bar{C}_v$ has a frequency-dependent component because of the possibility of time lag in attaining equilibrium in the vibrational, rotational and dissociation levels during the adiabatic process. As stated above, the experimental evidence indicates that in the case of air, a dispersion effect in the non-dissociation gas, if present, is negligibly small for the present purpose. In the case of carbon dioxide, on the other hand, an apparent lag in the vibrational equilibrium leads to dispersion at high frequencies.[10a]

The case of dispersion in dissociating gases has been studied by numerous workers[10b-e] for the $N_2O_4 \rightleftarrows NO_2$ reaction, but the complexity of the phenomena when the possibility of simultaneous changes in the vibrational, rotational and dissociation energy exists has interfered with an interpretation of the results in terms of a rate constant for the dissociation reaction. The rate constant has not been treated theoretically. Although the possible magnitude of the dissociation dispersion is small in the case of a gas like nitrogen tetroxide, where the molal dissociation energy is of the order of 14 kg. cal., it may be appreciable in some gases, including air at high temperature. The Einstein equation for the sound velocity is

$$c_f = \left[\frac{RT}{M}\left(1 + \frac{k_1^2 AB + \bar{C}_v R\omega^2}{k_1^2 B^2 + \bar{C}_v \omega^2}\right)\right]^{\frac{1}{2}}$$

where k_1 is the rate constant of the reaction in question, in the present instance dissociation, and A and B are given by

$$A = \left(\frac{2D}{T} - \bar{C}_v\right)\frac{1-\alpha}{1+\alpha} + R\ {}^{2\,-}$$

$$B = \left(\frac{D^2}{RT^2}\right)\frac{1-\alpha}{1+\alpha} + \bar{C}_v\frac{2-\alpha}{\alpha}$$

where D is the dissociation energy and α is the fraction dissociated. When f is 0 and ∞ we obtain

$$c_0 = \left[\left(\frac{RT}{M}\right)\left(1 + A/B\right)\right]^{\frac{1}{2}}$$

$$c_\infty = \left[\left(\frac{RT}{M}\right)\left(1 + R/\bar{C}_v\right)\right]^{\frac{1}{2}}$$

The frequency-independent component c_∞, is identical with c, and is tabulated in Table 1. From the dissociation data of this table and the preceding relations for c_0, we may calculate the ratio c_0/c_∞ of the low-frequency to high-frequency sound velocity. These values are given below for four significant temperatures.

Table 2.

T °K	c_0/c_∞
3000	.92
4000	.91
5000	.91
6000	.91

The difference between c_∞ and c_0 is thus somewhat less than 500° at a temperature of 6000 °K. In the ionization reaction this corresponds to a change of ionization potential of 1 volt in a mean ionization potential of 15 volts. The accuracy of the best available methods for measuring temperatures is limited by experimental consideration to about 300°. Thus in the case of the temperature range and the gases for which the dissociation dispersion is greatest, the effect is appreciable but not large. A critical examination of the temperature-ionization arc data, however, shows that for the steep pressure waves used in these experiments and described below, the dissociation equilibrium is probably not attained so that c_∞ data actually apply. This question could be decided with certainty if we had available, in addition to the sound velocity method, an independent means of measuring either the gas temperature or sound velocity in the region of dissociation dispersion. We have this independent means in the electrical method of determining the ionization temperature described in detail below. It is shown that from current density and voltage gradient data, one may calculate the equilibrium constant of the ionization equation. On the basis of an ionization potential assumed to be known for the arc gas, one may then determine an ionization temperature. If this ionization temperature were found to be above the gas temperature given by sound velocity measurements, the two possible interpretations would be (1) the ionization is not in equilibrium with the neutral gas; or (2) the velocity-temperature measurements are low by the amount of the dissociation dispersion. However, it is actually found[7] that for the case of refractory electrodes, such as carbon and tungsten, the ionization temperature and the gas temperature determined by sound velocity are identical within the experimental error of about 300 °C, corresponding to approximately .6 volt in the ionization potential. The best available evidence therefore, indicates that *for steep pressure waves* the ionization equilibrium does not follow the adiabatic cycle. If an accurate specification of the pressure wave were available, it would be possible to calculate a limiting value for the

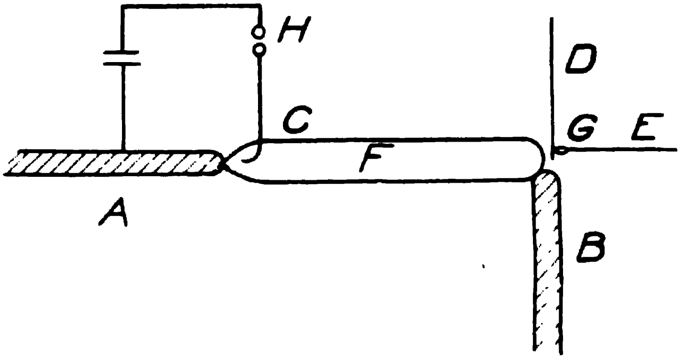

Fig. 3. Arrangement of electrodes for sound velocity measurement in arc. *H*, *C*, spark sound source; *D*, *E*, *G*, spark sound receiver.

rate constant of the dissociation process. With the data available, however, this calculation is hardly warranted.

Sound Velocity Measurement Methods. Two experimental methods of determining the velocity of sound in high-temperature gases have been developed in arc studies. In the first of these methods a single sound pulse originating in a spark discharge is passed through the high-temperature gas and received by a second spark acting as a microphonic device. It has been found that a spark sound source of this kind can be used directly in the hot gas of an arc column, and presumably as well at any lower temperatures. No "end correction" for a region of cool gas around the sound source is thus required. Although no sound receiver has been found which provides the same advantage, the best of a number of alternatives appears to be a low-current, high-voltage, non-oscillatory spark discharge. The discharge voltage exhibits a change during the passage of a sound wave which can be observed oscillographically. In Fig. 3 are shown schematically a spark sound source and spark receiver, together with auxiliaries in a gas column. In Fig. 4 is shown a cathode ray oscillograph record bearing four traces of the discharge voltage of the spark sound receiver. The time of passage of the sound wave through the high-temperature gas is indicated, the sudden increase in spark voltage to the right being in each case the point at which the sound reaches the spark. Reference should be made to the original papers for the details of the circuits.[7a,b] It should be remembered, in connection with both the sound velocity method and the density method of von Engel and Steenbeck, that the application of these principles of temperature measurement to lower temperatures, and particularly to larger gas volumes and longer measurement paths, could be made with

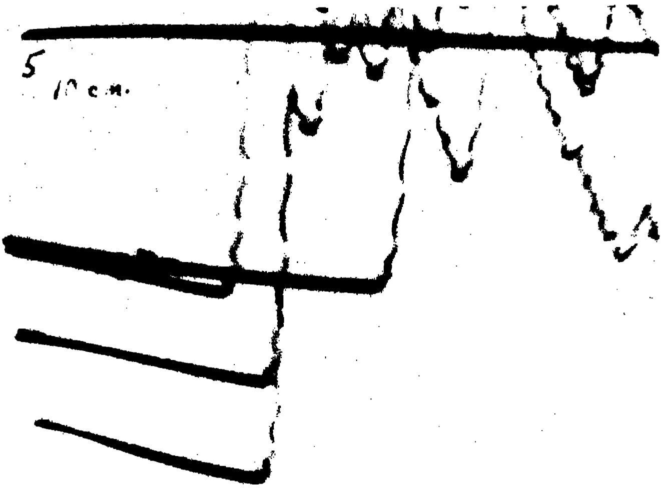

Fig. 4. Oscillogram of voltage of gap *G* (Fig. 3). Four traces are shown of the decay curve of the spark receiver; in each case the rise in voltage is due to the passage of the sound wave. In one trace (top, left) the voltage oscillation pickup from the sound transmitter is shown.

much greater convenience and simplicity in experimental method than in the relatively small columns of high-temperature arcs. For that reason the minutiae of the measurement technic as applied to arcs will not be stressed, since in most cases the physical principles might be applied with great simplification to other cases.

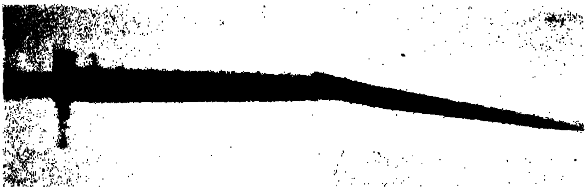

FIG. 5. Rotating mirror image of an arc column showing sound-wave front in luminous gas.

A second method of detecting the passage of a sound wave through a high-temperature gas rests on the observation that, if the gas is luminous, its luminosity will be higher in the region of high pressure associated with a sound wave. This effect can be observed very easily in an arc discharge where the high luminosity of the gas allows a photographic recording of the sound wave as a light wave. A record of this kind is shown as Fig. 5, which was obtained of a sound wave in an arc column by the rotating mirror camera arranged as in Fig. 6. Only exceptionally brilliant discharge columns can be photographed with sufficient time resolution to obtain an accurate measure of the sound velocity by this method, if the path is short, as in arcs. It is clear that, since with decreasing temperature the sound velocity will decrease by some power of the temperature which is less than one, while the light intensity will decrease much more rapidly than proportional to temperature, difficulties may be experienced in applying this measurement method to lower-temperature gases; but it is clear that, to the extent to which the path is greater and the required time resolution shorter, this difficulty disappears. The great increase in speed which is now available as a result of recent improvements in negative film emulsions will, of course, also greatly extend the possible range of application of the method. Analogous methods, however, which do not depend

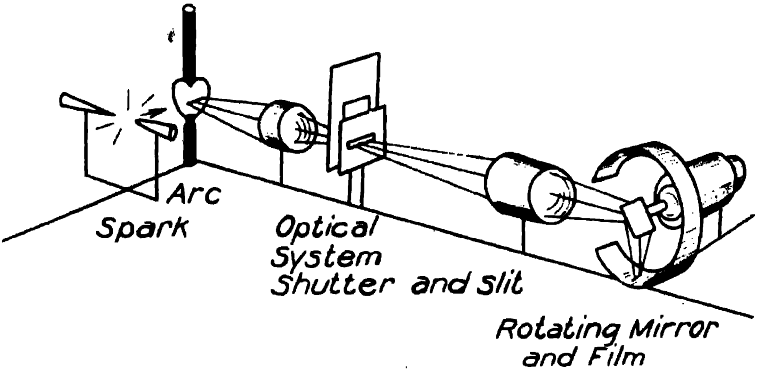

FIG. 6. Apparatus for photographing sound waves in arcs.

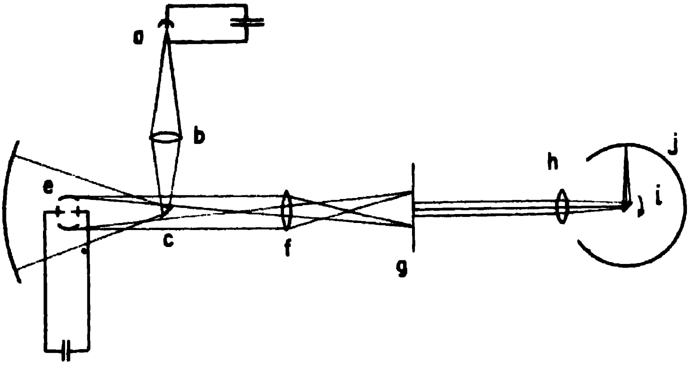

FIG. 7. Arrangement of optical system for recording schlieren sound-wave images with rotating-mirror camera.

upon the self-luminosity of the hot gas, are available in the schlieren method of Töpler,[11a] and the shadow method of Dvorak.[11b] Both of these methods depend upon the change in refractive index of the gas with temperature, while the light for recording is obtained from an auxiliary source. We have used both of them in conjunction with a rotating mirror camera to study abnormal sound velocities at room temperatures near the source of an intense spark discharge.[11c] The same method might be applied to a non-luminous gas at high temperature. Fig. 7 shows the arrangement of the schlieren apparatus, consisting of the spherical mirror, *d*, miniature plane mirror, *c*, lenses, *b* and *f*, and light source, *a*. The sound spark, *e*, is placed in the gas at the point at which the temperature determination is to be made. The refraction image of the expanding sound wave, which appears at the plane of the slit, *g*, is scanned by the rotating mirror, *i*, and stationary film, *j*. The lens, *h*, focuses the image of the slit, *g*, on the film, *j*. If the rate of energy input in the spark, *e*, is sufficiently great, the velocity will be abnormally great in the immediate vicinity of the discharge, the normal velocity characteristic of the gas temperature being reached at some centimeters distant. However, since the complete velocity-distance data are recorded by the method, the asymptotic "normal" velocity is readily determined.

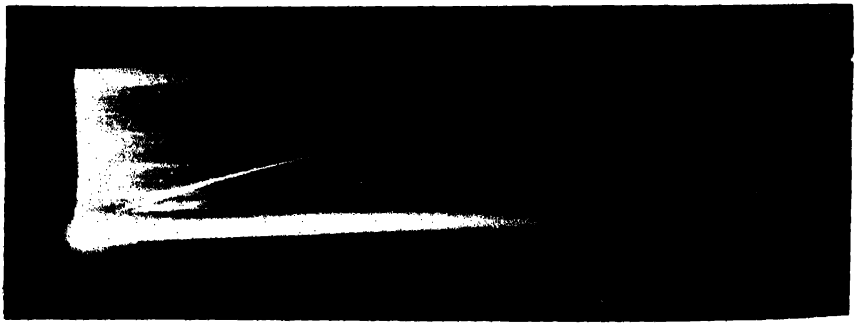

FIG. 8. Photograph, obtained by method of Fig. 7, of sound wave from 0.15 μf, 30-kv spark discharge.

In Fig. 8 is shown the schlieren-rotating mirror photograph of a single sound-pressure wave produced by a 30 kv, 0.15 μf spark gap in air at room temperatures. Minor wave fronts, up to and including that due to the fifth half-cycle in the damped oscillatory discharge, are visible in the original photograph.

So far as is known to the author, this method has not been applied to high-temperature gases.

Gas Temperature from Band Spectra

The attractive possibility of determining the temperature of a gas from its spectrum has been developed by Ornstein and his students in an extensive series of investigations.[12] The method has the advantage of exerting the least disturbance to the region of measurement and embodies the minimum requirements in the matter of length of gas path which can be explored.

Theory of Spectroscopic Methods. The basis of spectroscopic methods of gas temperature measurement rests upon the determination of relative intensities of lines originating in known energy levels within the atom or molecule.

If it is known or can be determined that thermal equilibrium exists, the relative intensities, I, of lines originating in a common ground state are proportional to the product of the Boltzmann factor $e^{-\epsilon/kT}$, the transition probability, p, and the *a priori* weight, a; thus

$$I = ape^{-\epsilon/kT}.$$

Here ϵ is the difference in energy levels corresponding to the lines in question. Although some atomic spectra might be used for this purpose, especially the principal series of alkalies, where the transition probabilities are known, the temperature determinations which have been reported have employed the vibrational and rotational bands of diatomic molecules, especially the rotational bands of CN and AlO. The CN spectrum has been so prominent in this work because it can be produced in the laboratory very simply and reproducibly in the low-current arc between pure carbon electrodes in air. A great many other diatomic molecules might be used for this purpose now that the technic and theory have been established for CN, but there are few molecular spectra which can be studied in the laboratory with the convenience and simplicity of the CN bands in the carbon arc in air. In arcs at atmospheric and higher pressure band spectra are extremely rare, and where found they tend to be somewhat fugitive. For example, the N_2 bands are found [13] in the low-current arc in air between polished water-cooled copper electrodes, but it is difficult to maintain electrode conditions sufficiently free from oxide for this purpose. As an alternative to using the spectrum of the gas, the temperature of which is to be measured, one may introduce a "foreign" molecule into the hot zone and make the temperature determination from its spectrum. From Al_2O_3 introduced into carbon arcs in this way the temperature in the relatively cool boundary layers has been determined from the O → O AlO bands. It would appear that the principal series of the alkali metals, for example lithium, might be used in the same way with the important advantage that spectrographic work can be done at low dispersion. On the other hand, low dispersion generally implies that the correction for change in plate sensitivity with wave-length must be taken into account. The transition probabilities are known for a number of alkali metals,[14,15] but the lack of this information for most elements is one of the difficulties in applying the method to other line spectra.

The application of the spectrographic method in the case of arcs can be illustrated by temperature determination in the core by the O → O bands of CN at 3883A. The band systems of CN as observed at low dispersion in the low-current arc between pure-carbon electrodes in air are shown in Fig. 9. The 3883.4Å band appears at high dispersion in Fig. 10,[16] as scanned by the recording microphotometer. The logarithm of intensity divided by the product of the transition probability and statistical weight is plotted as a function of the relative rotational energy. T is determined directly from the slope of the resulting plot, which will be a straight line if a Boltzmann distribution exists for the levels in question.

FIG. 9. Near-ultraviolet spectrum of arc between pure-carbon electrodes, showing cyanogen band system. (Wave length of band heads in Angstroms).

It is clear that the steps in the outlined process require a high order of accuracy at each point to avoid accumulative errors. Fig. 11 shows the log I/ap versus rotational energy plots for the CN O → O bands (Curves I, II, III, IV) from various orders of the gating spectroscope and the O → 1 band (Curve V). The lack of linearity at low term numbers is ascribed to ghost images in the grating.

In addition to CN, which has received the most study, some work has been done with AlO, C_2, CH, and the Balmer spectrum of H_2.

Measurement of Temperatures by Ionization

Some notes will now be included on the method which has been used to measure the highest known gas temperatures in arc columns.[17] To the objection that this method applies only to an electrical discharge column it can be replied that that is the only place the highest temperatures are found in terrestrial sources. Measurements of gas temperatures by sound velocity are in excellent agreement with the results of the band spectrum method of Ornstein, especially where the same experi-

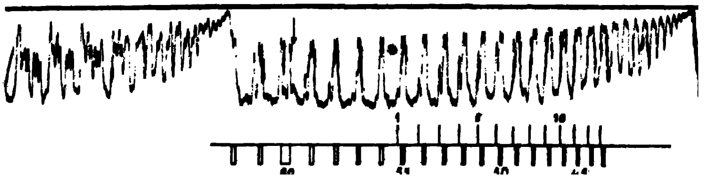

FIG. 10. Trace of a recording microphotometer film of the 3883Å band of CN at high dispersion (Brinkman).

mental conditions are reproduced. Since no knowledge of dissociation is required in the spectroscopic method, this agreement is in itself evidence that the dissociation equilibrium is established in the arc in atmospheric air. There is a good deal of additional evidence bearing on this point. Langmuir[18] found that in low-pressure hydrogen the dissociation products could be detected at relatively great distances from the discharge column, proving that the delay in the recombination mechanism *at low pressure* disturbs the equilibrium. Careful experiments with hydrogen and air arcs at atmospheric pressure have shown that this effect is negligible or absent at this pressure. This is to be expected on theoretical grounds because recombination processes (as, for example, that taking place as a three-body collision) are favored, and diffusion processes (due to the $1/p$ dependence of the *diffusion coefficient*) are subordinated at high pressure. All the evidence indicates that there is a complete thermal equilibrium in the arc in atmospheric air. The evidence that the ionization equilibrium is characterized by a temperature which is the same as the gas temperature comes chiefly from simultaneous measurements of arc temperatures by sound velocity and ionization density from electrical data. Consider the simultaneously measured gas temperature T (degrees K), arc diameter D (cms), current i (amps), and electric gradient E (volts/cm) in the discharge column. On the assumption that the current density is a constant across the section of the discharge column, which is a satisfactory approximation in many cases, especially in diatomic gases, we can obtain the average current density I

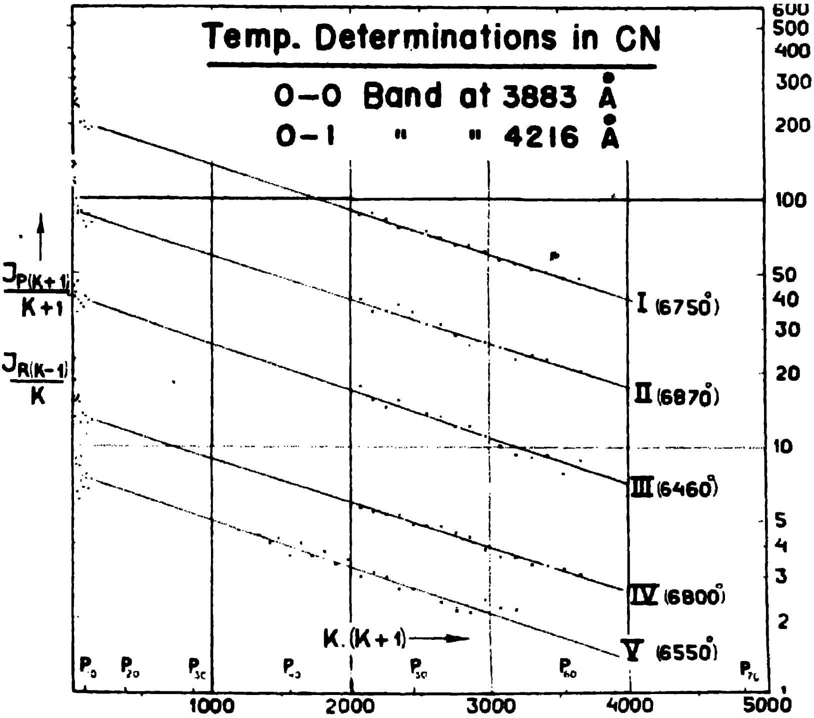

FIG. 11. Log $I/\nu p$ vs. $e^{-\epsilon/kT}$ plots of cyanogen bands (0—0 band, I, II, III, IV in different orders of the grating; 0—1 band, V).

(amps/cm²) from D and i. The quantity I is related to E through the conduction equation $I = n_0 e \mu E$, where e is the electronic charge, μ the electron mobility, and n_0 the electron density (cm^{-3}) at the temperature T. From the conduction equation we can obtain the expression

$$\left(\frac{n_0^2}{N}\right) = Ap\left(\frac{I}{E}\right)^2 \tag{6}$$

which relates n_0 and N (density of molecules at the temperature T in cm^{-3}) to the ratio of current density I and gradient E. A is a constant that depends upon the gas, and p is the pressure (atmospheres). Some values of A are given in Table 3.

Table 3.

Nitrogen (also air)	2.73×10^{10} ($p = 1$)
Hydrogen	0.76
Mercury	20.6

The left-hand member of Equation (6) can be used with the ionization equation

$$\log_{10}\left(\frac{n_0^2}{N}\right) = \log_{10} Ap\left(\frac{I}{E}\right)^2 = -\frac{5040 V_e}{T} + 1.5 \log_{10} T + 15.38 \tag{7}$$

to calculate for the ionization potential V_e of the gas in the discharge column the *ionization temperature* T. In cases for which this measurement has been carefully made, the ionization temperature T and the gas temperature T are identical within the limits of measurement. Since these test cases have been taken in arcs in air at atmospheric pressure, we may feel justified in assuming that the same is true at higher pressures. We have available, therefore, a method which, if applied with care, will allow a calculation of the gas temperature T in the discharge column from measurements of the electrical quantities I and E. This is, of course, far simpler than any direct measurement of T. From the way in which I and E enter in the relations it will be found that the accuracy of determining T is much greater than that involved in the measurement of I and E.

This measurement has been applied to arcs in high-pressure chambers where none of the other temperature measuring means could possibly be used.

Results of Arc Temperature Measurements

In Table 4 is tabulated a partial list of cases which have been studied by the temperature measurement method described above.

Table 4. Arc Temperatures Determined by Various Means.

T °K	Experimental Conditions	Method
5000 ± 400	3 amp arc in air	Density—x-ray absorption
5200 ± 450	3 amp arc in air	Density—x-ray absorption
6000	10 amps, in air	C_2 band at 5165 Å
5000	9 amps, in air	CN bands at 3883
6500	1–12 amps, in air	CN bands at 3883
4900–6300	Hydrogen, atm. pressure	Balmer lines
6550	7 amps, in air	CN bands at 4216 Å
5500 ± 150	50 amps, in air, cored carbon	Photograph of sound waves
4050 ± 200	6 amps, in air, long column	Oscillograph of sound waves
6440 ± 150	25 amps, tungsten, in air	Photograph of sound waves
6020	125 amps, welding arc, in air	Photograph of sound waves
4740 ± 150	43 amps, Na cored carbon	Photograph of sound waves
10,200	10 amps, air, 1000 atm.	Calculated from arc gradient and current density

It can be seen that many cases have been studied and that the results of the methods, which differ widely in principle, are in general agreement in showing that temperatures formerly thought to be present only in celestial sources are actually available in the laboratory.

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Concepts of Temperature in Electric Discharge Phenomena

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1. Introduction

Although the absolute temperature scale has been defined on the basis of the efficiency of a Carnot cycle, we now recognize a great variety of theoretical relations which might serve equally well to define the absolute scale. For the ideal case of temperature equilibrium, all the definitions should give the same temperature. If there is not equilibrium, the different definitions will in general lead to different values; but these different "temperatures" may still be convenient parameters to describe the physical state of a system. This extension of the concept of temperature to non-equilibrium is common in many fields of physics, but it has proved particularly useful in the study of electric discharges.

In an electric discharge, the positive ions because of their large mass and small velocity produce a positive space charge which holds the electrons in the space. The electric field of this space charge is limited to a thin sheath over the walls and electrodes, and in the rest of the space the electric fields are small and the numbers of ions and electrons per cm^3 are nearly equal. One has, in effect, an electron gas mixed with an atomic gas and an ion gas. This chapter deals with the state of these gases in a limited volume within which conditions can be considered as homogeneous, without considering the mechanism of the discharge as a whole. In an atomic gas, the state of the mixture can be described by the pressure and four different kinds of temperatures.

2. Electron Temperature from Probe Measurements

If a small electrode extends into the discharge the current voltage characteristics of this probe electrode serve to measure the properties of the electron gas.[1] At potentials positive to the space potential all electrons approaching the electrode are collected. At slightly negative potentials the slower electrons are repelled from the wire and the current decreases with increasing negative potential until only a positive ion current reaches the probe. Fig. 1 illustrates the current voltage curve for a low-pressure cesium discharge. The positive ion current can be extrapolated in a positive direction and the electron current is the algebraic difference between the total current and the ion current. When this electron current is plotted on a semi-logarithmic scale, the plot shown in the upper part of Fig. 1 is obtained. The intersection of the two lines comes at the space potential and the slope of the line on the left measures the energy distribution of the electrons. The fact that this semi-logarithmic plot is a straight line shows that the electrons have a Maxwell distribution of kinetic energy. For the case of electrons at a temperature, T, the current reaching a collector at a potential, V, would be

$$I = I_0 e^{-\epsilon V/kT} = I_0 e^{-11600\,V/T} \tag{1}$$

where I_0 is the current at $V=0$, ϵ is electron charge and k is Boltzmann's constant. Hence the currents at any two negative potentials determine T by the relation

$$T = \frac{5040(V_2 - V_1)}{\log I_1 - \log I_2} \tag{2}$$

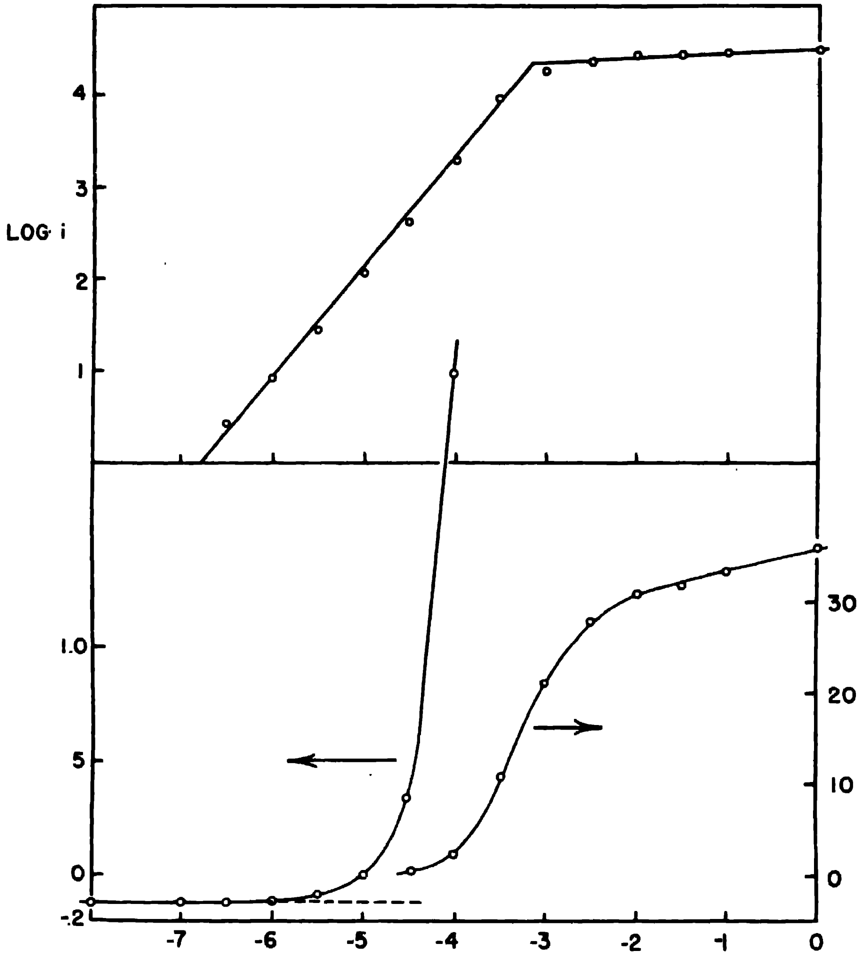

Fig. 1. Probe current in a cesium discharge (tube diameter 1.8 cm, current 2 amps, pressure .002 mm). Below are plots of current vs. potential relative to anode on 2 scales; above is a plot of log electron current vs. potential ($T_e = 4200$ °K).

In cases where the semi-logarithmic plot is linear, the slope of the line gives by Equation (2) a value of T which is called the electron temperature, T_e. In some cases, notably at very low pressures or close to the cathode, the electrons do not have a Maxwell distribution, and one cannot speak of an electron temperature.

The effective collecting area of the probe is equal to its actual area at the space potential, and the current density depends only on the number of electrons per cm ^{3} and on their velocity.

$$N_e = 4.03 \times 10^{13}\, i_e/T_e^{1/2} \tag{3}$$

where N_e is the electron concentration and i_e the current density. This relation is only valid at low pressures and when the current to the probe is a small fraction of the discharge current; and these restrictions limit the applicability of probe methods.

Fig. 2 is a semi-logarithmic plot of electron currents in a mercury discharge at three different positions along the radius of the tube.[2] The fact that the three lines are coincident at negative potentials shows that the temperature is constant and that the concentration gradient is related to the potential gradient by the Boltzmann relation:

$$N_1/N_2 = e^{11600(V_1-V_2)/T_e} \tag{4}$$

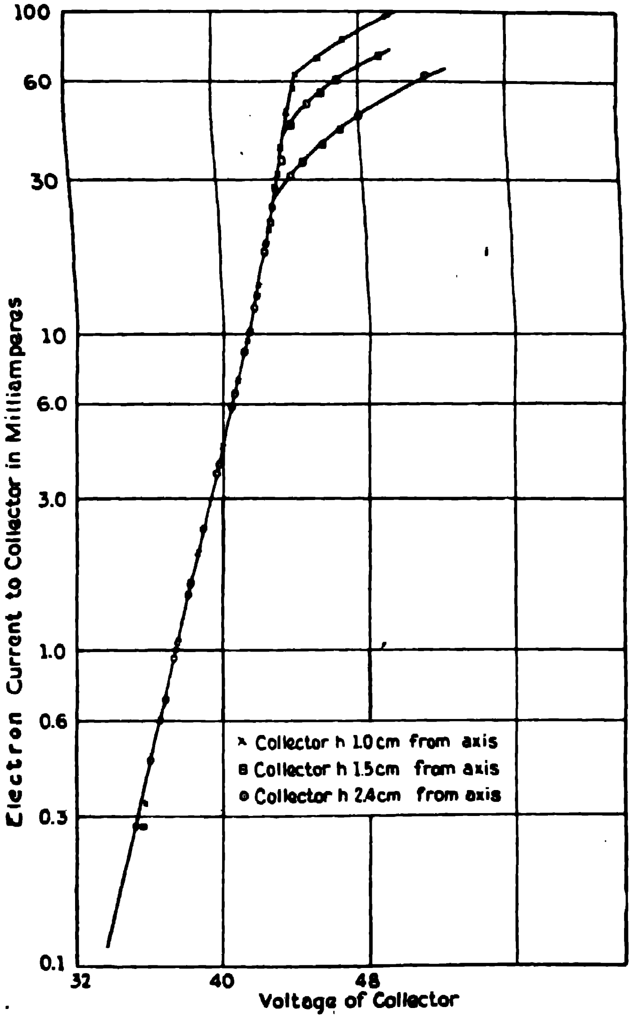

FIG. 2.

Semi - logarithmic plot of electron current in a mercury discharge (tube diameter 6 cm, current 5 amps, pressure .0054 mm). Probe at three positions 1.0, 1.5, and 2.4 cm from the axis (T_e = 19,900 °K).

where N_1 and N_2 are electron concentrations at points where the space potentials are V_1 and V_2. This result gives added significance to the view that the electrons can be considered as a gas at a temperature, T_e. The electron gas has a constant temperature but variable pressure.

Table 1. Summary of Electron Temperatures.

Gas	Current Density (amp/cm^2)	Pressure Range (mm)	Temperature Range (°K)
He[3]	.024	1 to 3	62000 to 56000
Ne[3]	.024	0.2 to 20.0	44000 to 16000
A[3]	.024	0.1 to 10.0	17000 to 8200
Hg[1,2]	.17	.0002 to .025	38000 to 12000
Na[4]	.02	.002 to .006	31000 to 29500
	.10	.002 to .006	19000 to 9600
Cs[5]	.80	.0012 to .33	4400 to 2500
		Mixtures	
Ne–Hg[6]	.3	5–.001 to .449	24000 to 7500
Na–Ne[4]	.02	.006–0 to 20	29500 to 6600
Na–Ne	.10	.006–0 to 20	9600 to 6600

Table 1 summarizes electron temperatures in different elements and mixtures. The temperature always decreases with increasing pressure. In mixtures of rare gases and metal vapors the spectrum is characteristic of the metal and the effect of the rare gas is primarily to decrease the rate of loss of ions by diffusion.

The variation of electron temperature with current density for cesium discharges

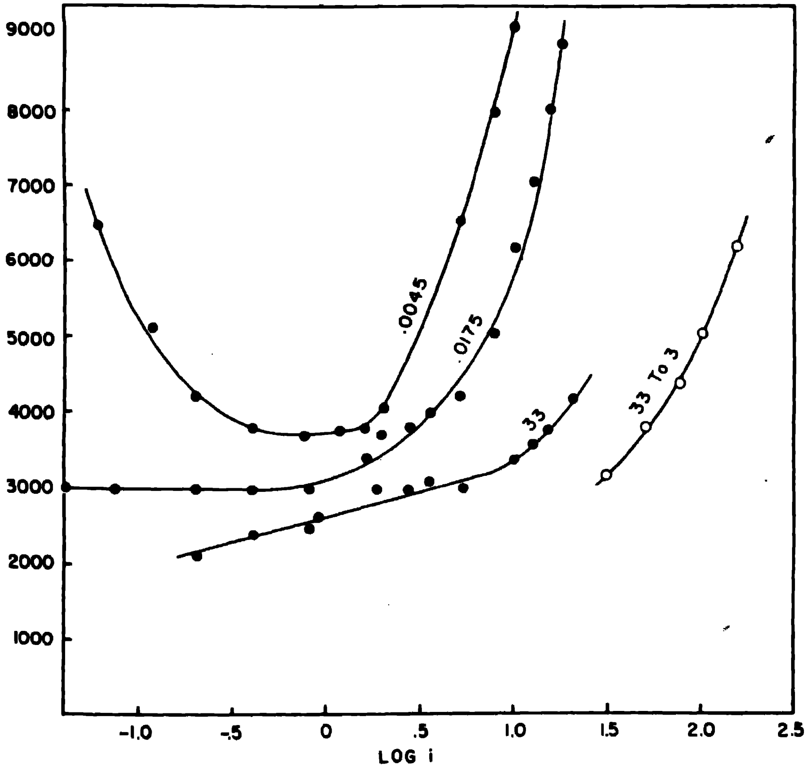

FIG. 3. T_e vs. log of current density for cesium at pressures in mm indicated on the curves. Dots give probe measurements in tubes 18 and 5 mm in diameter. Circles are measurements by a spectroscopic method in a 1-mm tube.[5,7]

at different pressures is shown in Fig. 3. The high temperatures obtained with very low pressures and currents involve a minimum power input and indicate that there is little interaction between the electron gas and the atom gas. At the other extreme a very high power input is involved. The input ranges from .04 to 3000 watts/cm^3 in the range of Fig. 3.

3. Gas Temperature

The subject of gas temperatures in electric discharges is covered in another report[8] and it is sufficient here to summarize some of the results. With pressures less than 1 mm, the gas temperature is not much greater than the temperature of the tube walls.[9] (Temperature differences range from 10 to 100 °C.) With pressure greater than this, the positive column tends to constrict and this effect is probably purely thermal and indicative of high gas temperature. Elenbas[10] has estimated the temperature in the constricted positive column of a mercury discharge at one atmosphere to be 6000 °K. In various arcs in air at one atmosphere temperatures range from 4000 to 7000 °K near the center of the positive column. In the constricted discharge the current density remains nearly independent of current, and at one atmosphere has a value of 3.5 amp/cm^2 in mercury vapor and values ranging from 10 to over 100 amp/cm^2 in different types of air arcs.

4. Positive Ion Temperatures

Probe measurements of the ratio of ion current to electron current indicate that ions reach a probe with kinetic energy comparable with the electron energy, but Tonks and Langmuir[11] show that this comes from a drift velocity toward the electrode and not from thermal agitation. Kinetic theory considerations indicate that for small mean free paths the temperature of ions must be nearly in equilibrium with the gas temperature. Fortunately it is known that the number of ions is nearly equal to the number of electrons and for most purposes it is not essential to know the ion temperature.

5. Radiation Methods of Temperature Measurement

A few general laws cover a variety of methods that make use of the spectral intensity distribution of a discharge to measure temperatures.[12] The number of quanta emitted per cm^3 per sec in a transition between states of quantum number n and n' can be expressed

$$J/h\nu = N_n A_{n,n'} \tag{5}$$

where J is the radiation flux in ergs per second in all directions in the absence of any absorption, N_n is the number of atoms per cm^3 in the excited state n, and $A_{n,n'}$ is the transition probability. If there is temperature equilibrium, the fraction of atoms in the state n is given by Boltzmann's equation:

$$N_n/N_1 = (g_n/g_1)e^{-E_n/kT} \tag{6}$$

where the g's are the statistical weights of the excited and normal states, E_n is the energy of the excited state and N_1 pertains to the normal state.

$$J/h\nu = (g_n/g_1)N_1A_{n,n'}e^{-E_n/kT} \tag{7}$$

If there is not equilibrium, Equation (5) remains true, and a measurement of J gives the value of N_n. Equations (6) or (7) may then be used to define a "concentration temperature," T_n, which is a measure of the relative concentration of atoms in the nth state.

Alternatively, the radiant energy at temperature equilibrium can be expressed as that of a blackbody times the emittance. Using the Wien approximation*

$$J(\nu) = \epsilon \frac{c_1}{\nu^3} e^{-h\nu/kT} \tag{8}$$

The emittance ϵ_ν for a uniform column of gas of length l is

$$\epsilon = 1 - e^{-al} \tag{9}$$

where a is the absorption coefficient per unit length. When there is not equilibrium (8) can be considered to define an effective temperature. Equations (7) and (8) are not independent relations but can be derived from each other by radiation theory, and it appears from the derivation that when there is not equilibrium the temperature defined by (8) must be the same as the "concentration temperature," T_n, defined by (6) or (7).

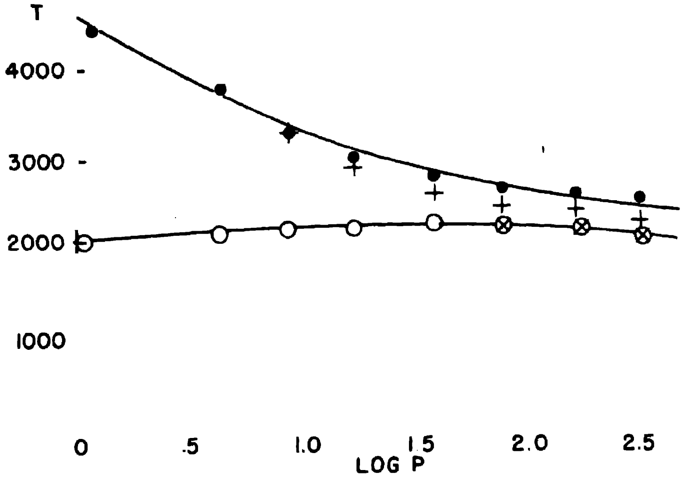

FIG. 4. Temperatures in a cesium discharge (tube diameter 1.8 cm, current 2 amps) vs. log pressure in microns. Dots are electron temperature, + indicates reversal temperature of the first doublet of the principal series, and × is the reversal temperature of its higher series lines. Circles are ionization temperatures (see section 11).

6. The Line-Reversal Temperature Method

If light from an incandescent blackbody is projected through a luminous discharge onto the slit of the spectrograph, then the line spectrum of the discharge will appear superposed on the continuous spectrum of the blackbody, and lines which are strongly absorbed may appear either as dark lines or as bright lines, depending on the temperature of the blackbody. The temperature at which the background matches a line is called the reversal temperature, and radiation theory [13,14] shows that this temperature is identical with what has been called more generally the concentration temperature. The method makes it possible to determine directly the concentration temperature without a knowledge of the constants occurring in Equations (6) and (7). For temperature equilibrium all lines should have the same concentration temperature, but for non-equilibrium different excited states will in general have different concentration temperatures.

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* Equations (5) and (8) are both approximations. Negative absorption must be included in Equation (5) for cases where Planck's law must be used rather than Wien's law.

In practice[14] a strip lamp calibrated in brightness temperature or the crater of a carbon arc is used instead of a blackbody, and the method is limited by the fact that most discharges operate at reversal temperatures above the range of these sources. Druyvesteyn,[15] in studies of the sodium discharge, has extended the range by placing a bulb of sodium vapor in the light path; and the author has used the device of photographing the spectrum with the discharge cut off during part of the exposure.[5,16] Both methods have obvious limitations.

Measurements on the first resonance doublet of cesium give values of the concentration temperature of the 6^2P state which are only slightly less than the electron temperatures. Values of 7^2P are somewhat lower, while values for 8, 9, 10, and 11^2P are less than for 7^2P and nearly equal to each other. Values for a 2-amp discharge as a function of pressure are included in Fig. 4.

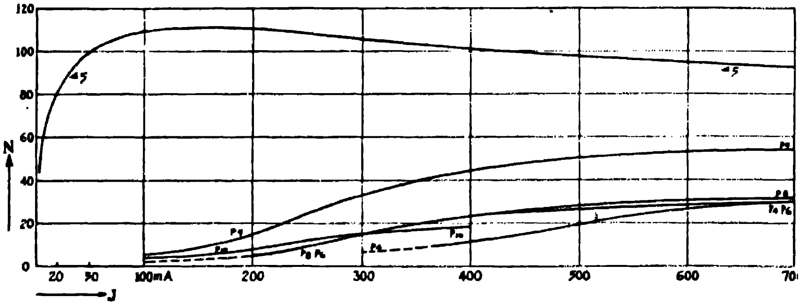

FIG. 5. Concentration of excited states (arbitrary units) vs. current as measured by anomalous dispersion in the neon discharge (tube diameter 8 mm, pressure 1 mm). The upper curve gives the first excited state, the lower curves give the second group of excited states.[17]

7. Anomalous Dispersion

Measurement of the anomalous dispersion in the positive column of a discharge is a very sensitive method of measuring the concentration of atoms in the final state of an emission line, and a study of the neon discharge by Kopferman and Ladenburg[17] is the best example of the method. Fig. 5 shows some results for a neon discharge at a pressure of 1 mm and a tube diameter of 8 mm. The upper curve is for the lowest excited state and shows that N_2 rises rapidly with increasing current to nearly a saturation value at a current of 100 ma. The lower curves pertain to the second group of excited states, and N rises gradually and approaches saturation at 700 ma. The upper curve gives by Equation (6) a concentration temperature of 20,200° ± 10 per cent. The higher states reach a temperature of roughly 23,000° at 700 ma. Seeliger and Hichert[3] give values of electron temperature of 26,000° at 100 ma and 22,000° at 300 ma, but these values pertain to tubes of diameters 2 and 4 cm. At a pressure of 9 mm the concentration temperature of the lowest states is 15,000° and the electron temperature is 16,000 °K. At the lower pressure the gas is only slightly heated by the discharge yet the degree of excitation corresponds to a temperature of 20,000°. The lowest excited state is one of a group of four states two of which are metastable, but both radiating and metastable states have nearly the same concentration temperatures for currents of 100 ma or more.

8. Relative Intensity Measurements

In most applications of Equation (7) to measure temperature, the intensity ratio of two lines is used. If there is temperature equilibrium, the ratio involves a factor $e^{-\Delta E/kT}$, where ΔE is the difference in energy of the two initial states. If there is not equilibrium and the two concentration temperatures differ, the method fails as it gives only one relation between two unknowns. The best illustration of the method is the determination of "rotation temperature" from the intensity distribution in the rotational structure of a band which is described in another report.[8]

Ornstein and his colleagues have used the relative intensity of the Balmer lines to measure the temperature of a hydrogen arc [18] and the intensity ratio of a widely separated doublet of gold to measure the temperature of a carbon arc in air containing a trace of gold.[19] The resulting temperatures are equal within experimental error to the gas temperatures. The author [20] has used the relative intensity of the higher series lines of cesium to measure the temperature assuming that within each series A is inversely proportional to n^3. At pressures above .03 mm, the results agree with measurements obtained by the reversal temperature method and indicate that all the higher states have the same concentration temperature. At low pressures this is not true. Barnes and Adams [21] have made a similar analysis of the spectrum of a mercury arc at pressures up to 500 mm, and results indicate that in this case the concentration temperature is not the same for different states.

9. Absolute Intensity

In an intense discharge the gas is quite opaque at wave-lengths coincident with the strongest lines, and it is possible to use Equation (8), taking $\epsilon=1$. The measurement $J(\nu)$ involves measuring the energy radiated by the line and the line width. Adams and Barnes [22] have applied the method to a mercury arc at 500 mm pressure and find that the lines 5461A, 4358A and 4047A each give about 6000 °K for the concentration temperature of the $7S$ state. Fortunately the value of T is quite insensitive to errors in the estimate of the line width, and the method is particularly valuable for very intense discharges.

Anderson [23] has investigated the intensity of the continuous spectrum emitted in a powerful condenser discharge through air at low pressure (maximum current density 150,000 amp/cm^2). The ionized gas is completely opaque and Equation (8) can be used with $\epsilon = 1$; but the radiant energy does not have a temperature distribution. The relative intensity between 8000 and 4000A would indicate $T = 10{,}000$ °K, but the absolute brightness indicates temperatures varying from 52,000 to 19,000 °K between 7000 and 3500A. Since the initial states for the radiation are free electrons and ions, the results suggest that the electrons do not have a Maxwell distribution.

10. The Recombination Spectrum

The continuous spectrum extending from each series limit to shorter wave-lengths results from free electrons recombining into the state corresponding to the series limit. The intensity is proportional to the square of the electron concentration and the intensity distribution depends on the electron temperature. For the band extending beyond the $6P$ limit of cesium, the energy radiated per cm^3 per second in unit wave-length range is

$$\lambda J(\lambda) = (.516 \times 10^{-18} N_e^2/T_e^{3/2})e^{-E/kT} \qquad (10)$$

$$E = hc(1/\lambda - 1/\lambda_0)$$

where λ is the wave-length observed and λ_0 is the series limit.[7] This equation has been used to measure N_e and T_e in very intense cesium discharges in capillary tubes. Fig. 3 includes some data on electron temperature obtained by this method. For most elements the coefficient of Equation (10) is not known.

11. Electron Concentration

Sections 2 and 10 describe two methods of measuring electron concentration: measurement of the current density to a probe wire, and measurement of the intensity of the recombination spectrum. Another method depends on the relation between potential gradient and current·density in the uniform positive column.[2] The ratio of these is related to the concentration of electrons and atoms as follows:

$$X/i = 2.94 \times 10^9 T_e^{1/2} N_1 S_1 / N_e \tag{11}$$

where S_1 is the effective atomic scattering area. (The scattering area of ions must be included in (11) if more than 1 per cent of the atoms are ionized.) The method has frequently been used to measure N_e in arcs at atmospheric pressure.[24]

In an intense discharge the lines near the end of a series broaden out and fuse together because of ionization broadening. The effective quantum number of the last line of a series depends only on the electron and ion concentration. Experiments on the D and F series of cesium give the relation:

$$\log N_e = 23.06 - 7.5 \log n_m \tag{12}$$

where n_m is the effective quantum number of the last line.[25]

Theoretical considerations [26] indicate that this equation will be a good approximation for other elements and other series, and it offers an insensitive but simple method of determining N_e in any intense discharge.

12. The Saha Equation

For the case of temperature equilibrium the ionization of a gas is given by Saha's equation, which for a single stage of ionization can be written [27]

$$\frac{N_e N_+}{N_1} = 2.43 \times 10^{15} \frac{2g_+}{g_1} T^{3/2} e^{-E_i/kT} \tag{13}$$

where $2g_+/g_1$ is the ratio of the statistical weights of the ionized state and the normal state (the ratio is one for the alkalies and hydrogen) and E_i is the ionization energy. For most discharges $N_e N_+ = N_e^2$. When there is not equilibrium, values of N_e^2/N_1 define an effective temperature which may be called the ionization temperature.

Elenbas [28] has used the gradient in the A. C. mercury arc at 1 atmosphere to measure the ionization temperature; and the value of 6400 °K at the center of the positive column is equal within experimental error to the gas temperature, 6000° ± 800 °K.[10] The gradient in the mercury arc at 200 atmospheres (a constricted discharge in a tube 1 mm in diameter) indicates a temperature of 8900 °K.[29] It required a power input of 1400 watts per cm of length, or nearly 200 kw per cm,[3] to maintain this temperature.

Studies of arcs in air indicate that here, too, the ionization temperature is nearly equal to the gas temperature; but the analysis is complicated because there is a mixture of gases of uncertain composition.[8] Mankopff [30] has used the device of putting a trace of calcium and magnesium in the arc and measuring N_+/N_1 for both elements by means of the relative intensity of arc and spark lines using Equations (7) and (13).

In this case N_e of Equation (13) is the total number of electrons while N_+/N_1 and the constants on the right pertain to calcium or magnesium. Values for two elements give both T and N_e.

The values $T \approx 6400$ °K and $N_e = 10^{16}/\text{cm}^3$ pertain to the negative glow close to the cathode of the carbon arc. If there is not temperature equilibrium and the ionization temperatures of the two elements differ, this method of analysis fails.

Values of the ionization temperature in cesium for conditions far from equilibrium are included in Fig. 4.[31] It is found that the ionization temperature is equal within experimental error to the concentration temperature of the higher excited states. The ionization temperature at constant current is nearly independent of pressure. In the mercury discharge at .17 amp/cm^2 the ionization temperature remains nearly 4000° in the pressure range .0002 to .025 mm, while electron temperatures range from 38,000 to 12,000°. The ionization temperature increases with current density and an extrapolation indicates that at 3.5 amp/cm^2 it would be about 5000 °K. The constricted arc at 1 atmosphere operates at this current density and an equilibrium temperature of about 6000 °K. The comparison shows that with a millionfold change in pressure, the ionization temperature changes very little.

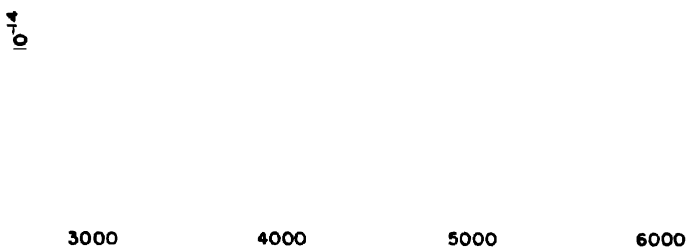

FIG. 6. Number of electrons per cm^3 vs. electron temperature for a cesium discharge at a pressure of .33 mm. Circles give observed values in a tube 1 mm in diameter; the curve gives the theoretical values for temperature equilibrium at this pressure.

Measurements of electron concentration and electron temperature in the cesium discharge at very high current density[7] are shown in Fig. 6 as a plot of electron concentration versus electron temperature at constant pressure. (The relation between temperature and current density is given in Fig. 3.)

The number of electrons reaches a nearly constant value because the atoms are nearly all ionized. A further increase of temperature then tends to decrease the number of ions and electrons by Charles' Law. The number of electrons that would exist in temperature equilibrium at a total pressure equal to the vapor pressure is shown by the curve of Fig. 6 and the agreement between the observed points and the curve gives direct evidence that there is nearly temperature equilibrium. At lower pressures the gas temperature and ion temperature remain below the electron temperature even at the highest current densities.

Conclusion

Four different kinds of temperature and the gas pressure are required to describe the conditions in a discharge in a monotomic gas:

(1) the electron temperature which gives the kinetic energy of the electrons;

(2) the gas temperature which gives the number of atoms per cm^3;

(3) the concentration temperatures which determine the population of the different excited states;

(4) the ionization temperature which gives the number of electrons per $cm.^3$ Since the number of ions is equal to the number of electrons, it is not essential to specify the ion temperature. In a molecular gas dissociation, vibration and rotation involve additional temperatures.

At low pressures and currents the electron temperature is high and all the other temperatures very low. With increasing current and pressure the electron temperature drops and the concentration temperature of the first excited state rapidly rises until the two are nearly in equilibrium. The ionization temperature at constant current density is nearly independent of pressure, while the electron temperature decreases with increasing pressure and gradually approaches it. The constancy of the ionization temperature implies that N_e^2/N_1 is constant at constant current density. The gas temperature remains low with increasing pressure until the discharge becomes constricted. It then rises and approaches equilibrium with the other temperatures at one atmosphere (or much less if the current density is high). The constricted discharge operates at a current density which is independent of the current and increases with increasing pressure. The ionization temperature increases with increasing pressure and N_e/N_1 remains constant.

With increasing pressure and current the elementary interactions in a discharge become increasingly complicated, but the description in terms of temperatures becomes progressively simpler and finally one temperature suffices to describe the conditions. The use of four kinds of temperatures at lower pressures is required because the phenomena are inherently complicated.

Most of the methods of temperature measurement involve no assumptions as to the mechanism of the discharge and some of them are equally applicable to measurement of flame temperatures and stellar temperatures. Reports on stellar temperatures and flame temperatures cover some of these topics in more detail.

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Magnetic Cooling; Production and Measurement of Temperatures Below 1 °K

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Giauque[1] and independently Debye suggested in 1926 that by use of a large magnetic field, one could cool certain paramagnetic salts below the temperature available with liquid helium. Giauque and MacDougall[8] at the Berkeley Laboratory were the first to overcome the experimental difficulties and realize temperatures well below 1 °K. Shortly thereafter, at Leiden by de Haas and Wiersma, and at Oxford by Kurti and Simon, similar results were reported. Temperatures of the magnitude 0.001 °K have been produced by these laboratories; on the other hand, temperatures down to 0.01 °K have been measured and identified with the Thermodynamic Temperature Scale. It will be the purpose of this article to present a discussion of the experimental and theoretical research on the production and measurement of temperature in the region below 1 °K. A list of references, grouped as to subject, will guide the reader in a more comprehensive study.

A. Low Temperatures and the Creation of Order

We must begin an explanation of the magnetic cooling effect by examining the thermodynamic principles behind the production of low temperatures. The experimenter wishes to lower the temperature of a system which is in some phase and composed of atoms, electrons, etc. There is a supply of energy (electrical or mechanical) with which he may operate on the given system. It is an every-day experience that the supply of energy could be allowed to dissipate itself into the system and so increase the temperature. This spontaneous natural process which gives the system extra energy also increases the entropy in accordance with the second law of thermodynamics. Entropy is an index of the degree of disorder of the system and for our discussion is as important as the role of energy. For example, our system might have been ice which the energy had transformed to water and then steam. The molecules locked into the crystalline pattern constitute order; in the vapor phase, disorder. We may, therefore, expect difficulty in attempting to lower the temperature of the system since this means, besides removal of energy, a creation of order in the system. However, entropy is a statistical quantity and is a function of parameters such as temperature, volume, and electromagnetic fields. Thus, if the entropy may be influenced by one of these parameters (other than temperature of course) we may look for a thermodynamic process which will leave the system in a state of order, and so with a lower temperature.

B. Lowering Entropy of a Gas by Compression

Let us consider the process of liquefaction of a gas such as hydrogen, so that these principles may be illustrated. The supply of energy available to the experimenter is used to compress the gas to about 100 atmospheres. This process is done isothermally (in practice, of course, it is pre-cooled to liquid nitrogen temperatures) and then the gas is allowed to expand without thermal contact with its surroundings. The expansion causes a drop in temperature and, by letting the cool gas pass out of the expansion chamber in such a way as to pre-cool the incoming gas, liquefaction soon begins.

The compressor has lowered the entropy because the system has been squeezed into a small volume without change of temperature. For the physicist, trained in the concepts of statistical mechanics, it is more accurate to state that the distribution of the system in phase space (*i. e.*, momentum-volume space) has been squeezed into a narrow region. Entropy is proportional to the width of the region the system occupies in phase space. Fig. 2 shows the entropy-temperature diagram for cooling a gas by isothermal compression followed by adiabatic expansion. The thermodynamic definition of entropy change is

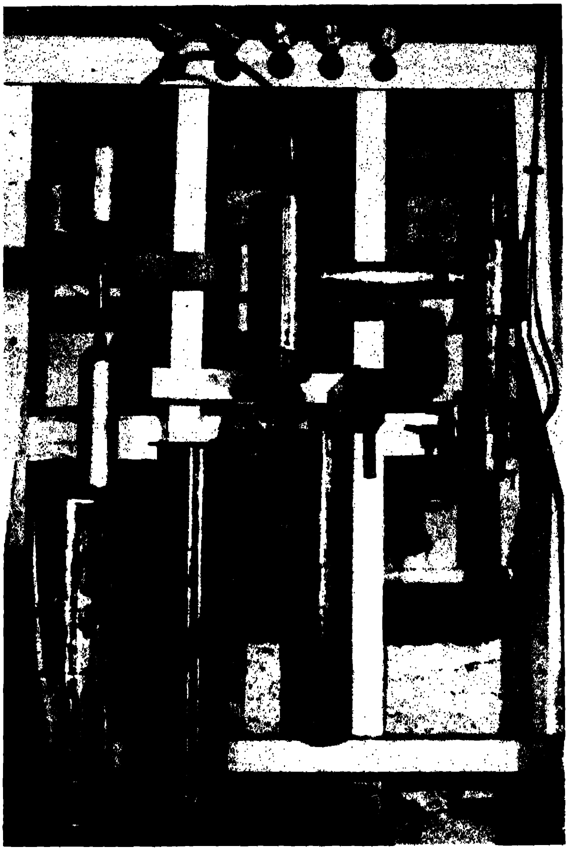

Fig. 1. Hydrogen Liquefier.

$$\Delta S = \Delta Q/T \tag{1}$$

where ΔQ is the heat change in the process (considered as perfectly reversible) and T is the absolute temperature. We shall presently consider this equation as the definition of temperature and make use of it to determine the temperature scale below 1 °K. During the adiabatic expansion there is no thermal contact, *i. e.*,

$\Delta Q=0$, and hence the absolute value of the entropy remains unchanged. The semblance of order which was given to the system by the volume parameter has now been taken over by the temperature.

C. Lowering Entropy by a Magnetic Field

By pumping the vapor phase away, the liquid hydrogen produced above can become a solid with a consequent lowering of temperature. But this is the limit for this system, since the solid represents order. These remarks bring out the important features behind the production of temperatures below 1 °K. For the new region, we must find a system which is still in a state of disorder at 1 °K and a parameter (other than temperature) with which we may bring the disorder into a state of order. Such a system is to be found in those paramagnetic salts whose internal magnetic dipoles show a random spacial orientation even at 1 °K. This arbitrariness of orientation on the part of the dipoles (or more properly the electron spin moment) constitutes a degree of disorder, and it may be brought into a degree of order by means of a magnetic field. Thus a magnetic field is the parameter which squeezes the entropy to a lower value. The transfer of the newly created order in the system from the magnetic field parameter to the temperature parameter is entirely analogous to the S-T diagram for gases in Fig. 2. An adiabatic demagnetization constitutes the transition B to C which was formerly an adiabatic expansion of the gas.

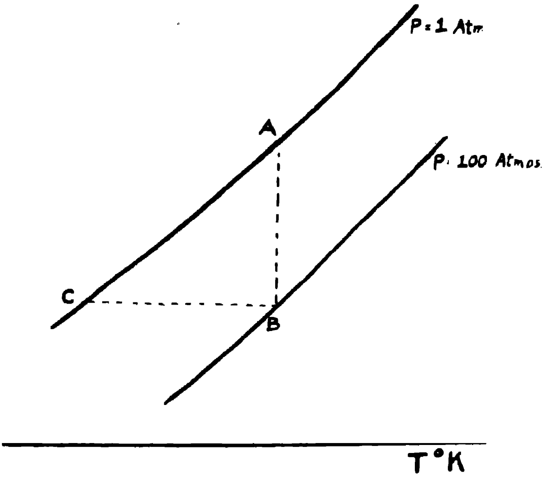

FIG. 2. Entropy temperature diagram for cooling a gas. Isothermal compression (A to B) is followed by adiabatic expansion (B to C).

In Fig. 3 we see a photograph of the cryostat of Professor F. Simon as it appears between the pole pieces of the giant electromagnet of the Academy of Science, Paris, France. Capable of producing fields of as much as 60 kilogauss, this laboratory has produced temperatures below 0.01 °K. In order to indicate the essential features of the procedure, we show in Fig. 4, a sketch of the experimental chamber. Liquid helium at 1 °K is in the double-wall section, and the paramagnetic salt, $Fe(NH_4)(SO_4)_26H_2O$, is placed within the space so formed. A number of suitable salts have been used by experimenters; Professor Giauque first used the hydrate of gadolinium sulfate. The pole pieces are shown in the figure, but the entire upper portion of the apparatus, the outer liquid hydrogen Dewar flask, etc., are omitted.

Three tubes lead into the cylindrical chamber from the upper portion of the apparatus. Two of these lead into the helium chamber and are for the purpose of (1) condensing the helium into the chamber, and (2) measuring the vapor pressure of this helium in order to know the temperature of the bath. Keesom and co-workers at Leiden[17] have established this convenient vapor pressure-temperature relationship. The third tube (3) is to allow helium gas to pass into the space about the salt so that it may serve as a heat exchanger while the powerful magnetic field is on. After the heat of magnetization has been removed, *i. e.*, the quantity ΔQ of Equation (1), the "heat exchange gas" is pumped out and an adiabatic demagnetization is the result of turning off the magnetic field. The entire process of getting the heat of magnetization out of the salt, *i.e.*, of getting both salt and bath back into a state of thermal equilibrium at 1 °K, and of completing the demagnetization, requires about 20 minutes. A flowmeter on the evaporating gas from the helium

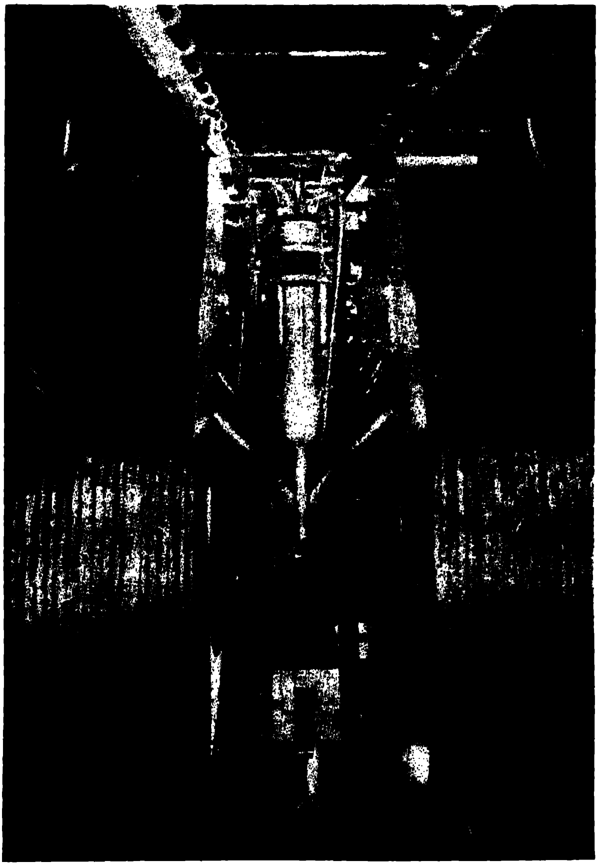

FIG. 3.

bath indicates that the heat of magnetization has been removed when it returns to its normal reading. It is impossible to convey in a brief article an idea of the enormous amount of precision "plumbing" associated with cryostats of this type.

D. How Low Will the Temperature Drop?

The general thermodynamic process of influencing the entropy by means of a magnetic field and so lowering the temperature of the paramagnetic salt should be clear from the foregoing paragraphs. The questions of how the field accomplishes this and of what the end temperature will be for any given salt next present themselves. Such a detailed question of the system requires a detailed description of the properties of the system.

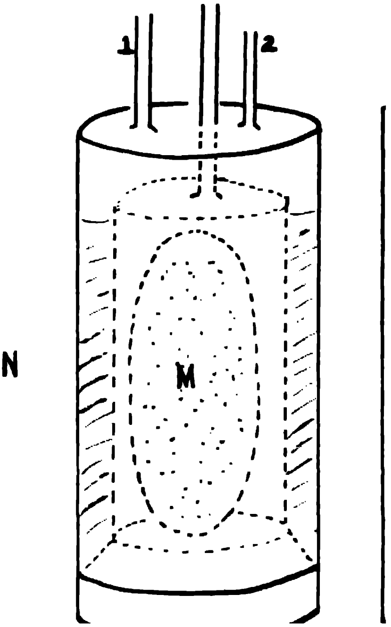

FIG. 4. Cryostat for magnetic cooling.

In the case of iron ammonium sulfate, there are five electrons in the Fe ion which constitute the magnetic dipoles. At 1 °K we may picture these dipoles as having a random spacial orientation. This disorder may be removed by the alignment of the dipoles with the direction of the external magnetic field. However, this creation of order by a magnetic field may be identified with the Zeeman effect. New energy states are created and the electrons move into these new states.*

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* It is more accurate to think of the disorder as being connected with the fact that the five electrons exist in one energy state, *i.e.*, a degenerate energy state. The degeneracy is removed by an external magnetic field because the single state is split into several states. This is similar to the splitting of states observed in the Zeeman effect.

In describing an energy state we make use of so-called quantum numbers; among these is the magnetic quantum number which is made up of the spin and orbit momentum

In Fig. 5 we show on the entropy-temperature diagram the value at 1 °K for the entropy of Fe-alum which arises from the disorder in the dipoles. The contribution to the entropy arising from the lattice vibrational energy is negligible at these temperatures. We may now make use of the Nernst law and say that at the absolute zero of temperature the entropy of the salt is zero. Thus on lowering the temperature we may expect that the salt will, of itself, lower the entropy, and so we may draw some seemingly arbitrary connecting curve as in Fig. 5. If the salt itself is to remove the degeneracy of the electron state, we must expect electric and magnetic forces within the crystal to become influential somewhere between 0 and 1 °K. In salts where these forces are strong, then their influence causes a drop in entropy at a temperature which is up toward 1 °K.

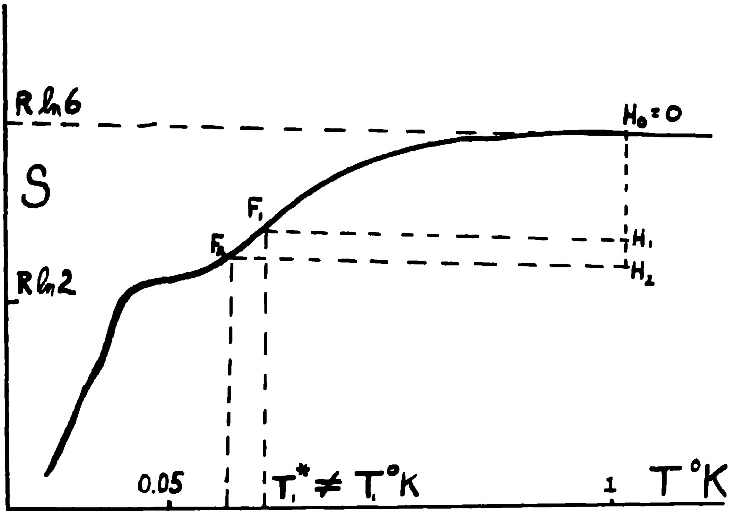

Fig. 5. Entropy-temperature diagram for magnetic cooling.

The entropy-temperature curve in Fig. 5 is for zero external magnetic field. The adiabatic demagnetization process which has been discussed in the earlier paragraphs may be followed on this diagram. Starting at 1 °K, a magnetic field is turned on such that the salt remains in thermal contact with the liquid helium at 1 °K. The entropy is lowered by an amount proportional to the magnetic field intensity (see appendix of this article). An adiabatic demagnetization from this point means that the entropy remains constant; thus the temperature falls to such a value as corresponds to the entropy-temperature curve in zero magnetic field. We have thus answered the question of how far the temperature will drop. It is clear that the magnitude of the interaction forces determines where on the temperature coördinate the entropy begins to diminish. Thus the lowest temperatures are to be obtained by those salts which are magnetically dilute, *i.e.*, the para-

quantum numbers of the electrons in the state. In the case of Fe-alum, the 5 electrons will give rise to 6 magnetic quantum numbers: $m = \pm 5/2, \pm 3/2, \pm 1/2$ and the single degenerate energy state will split up into 6 energy states in the presence of a magnetic field. These new states will be in energy units greater and smaller than the original state as given by the expressions: $\epsilon = \pm 5\beta H, \pm 3\beta H, \pm \beta H$, where β is the Bohr magneton. The entropy per mol for this six-fold degeneracy is: $S = R \ln 6$.

magnetic ions are far apart so that their interaction is indeed feeble. This is entirely analogous to the way that He gas liquefies at a lower temperature than H_2 gas because the interaction (van der Waals) forces are so feeble.

E. The Interaction Forces

A few words concerning the origin and nature of the above-mentioned "entropy squeezing" forces, will clarify what follows on the determination of temperature. Let us consider Fe-alum. The alum crystallizes in the cubic system; the Fe and (NH_4) ions form a "rock salt" lattice and the 6 water molecules are placed octahedrally around the cell. The SO_4 ions are within the unit cell and thus compensate the total electrostatic charge to zero. The Fe^{+++} ion thus exists in a crystalline electric field, and we may expect such a field to interact with the degenerate electron state of the Fe^{+++} ion, *i.e.*, influence the order of the dipoles. Since each Fe ion constitutes a magnetic dipole, it will cast a magnetic field on its neighbors. A distant neighbor is another Fe ion and we may expect a feeble interaction between the magnetic dipoles.

The interaction forces arising from these two sources will serve to bring the entropy of the alum from a value $R\ln 6$ at 1 °K to a value approaching zero as the temperature is lowered to 0 °K. The possibility of a further type of interaction, namely, an exchange force between the dipoles, can perhaps not be completely neglected. The magnitude of these interaction forces depends upon the particular characteristics of the paramagnetic salt. Thus also the temperature at which the forces are able to lock the system into a state of order is a particular characteristic of the salt. In Fig. 5 the drop in entropy occurs in two steps: (a) when the kT energy of the crystal becomes equal to the electric field, and (b) equal to the magnetic interaction energy.

It is very instructive to have some idea as to the entropy changes brought about by the interaction forces. Starting from a value $R\ln 6$, the crystalline electric field can only partially remove the degeneracy because there is left at least a twofold degeneracy corresponding to the parallel or anti-parallel orientation of the dipoles to a possible external magnetic field.[26] Thus the entropy is lowered to $R\ln 2$ by the electric field. The effect of the magnetic coupling is to lower the entropy even further. Before this action sets in one may consider the salt as composed of N independent paramagnetic ions. After the coupling action sets in, the crystal behaves like a giant molecule which has a single lowest energy state. This single lowest energy state may possibly be z-fold degenerate; but in any case $z \ll N$ and so the entropy falls to the nearly zero value: $S = k\ln z$, where k is the Boltzmann constant.[28]

F. Magnetic Thermometer Below 1 °K

The establishment of an absolute temperature scale in this new region has been one of the major problems for experimenters. The measurement of temperature in general is made possible through the regular (if not linear) behavior of some physical parameter with a change of temperature. Thus the change in pressure of the constant-volume helium gas thermometer serves as a temperature indicator. But this thermometer becomes awkward at liquid helium temperatures because the gas no longer behaves sufficiently regularly. This is an important point: the failure of thermometers in temperature regions where interaction forces destroy ideal behavior. In the region below 1 °K the only parameter which behaves regularly (and which can still be easily measured) is the magnetic susceptibility of the salt used in the new cooling process. However, at sufficiently low temperatures, even this thermometer departs from ideal behavior.

In Fig. 6 a simplified electrical circuit is shown for the measurement of the magnetic susceptibility of a salt (M) within the cryostat. The salt is both its own refrigerant and thermometer. The switch is closed to send a current through the primary (P) such that a magnetic field of several gauss is created. The two secondaries, S_1 and S_2, are wound equal and opposite to each other. In the absence of a paramagnetic salt the induced emfs in the secondaries are equal and opposite so that the galvanometer (G) shows no deflection. However, when the paramagnetic salt (M) is placed within S_1, the induced emf of S_1 is increased, so that the galvanometer receives a ballistic throw. The throw of the galvanometer for a given current in the primary is thus proportional to the susceptibility of the salt. The coils of Fig. 6 are kept in liquid hydrogen to lower their resistance and so make the measurements possible with an ordinary galvanometer. The salt (M) is, of course, deep-nested within the cryostat, as shown in Fig. 4. The current in the primary coil may be reversed by a suitable switch for studying hysteresis effects in the salt. An external constant magnetic field may be superimposed on the induction system. Most workers have used alternating current in a modification of the circuit shown here. Giauque has also maintained a small steady field and the change of induction with temperature was measured with a potentiometer across the leads of the secondary.

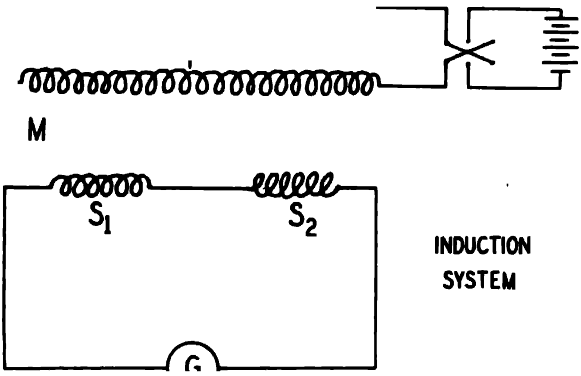

FIG. 6.

The magnetic susceptibility, χ, of the salt is the number of dipoles per unit volume per unit magnetic field exerted on the salt. The classical view was that in a solid one had a certain density of magnetic dipoles and all or part of these could be oriented by an external magnet. The experimental fact that the lower the temperature of the solid the easier for the external field to orient the dipoles led to the Weiss-Curie Law:

$$\chi = C/(T - \Theta) \tag{2}$$

where C is Curie's constant (a characteristic constant for each salt studied) and T the absolute temperature. Θ is a temperature constant and is given by the intersection of $1/\chi$ with T axis. For salts used in magnetic cooling, Θ is approximately zero. It is not the damping of atomic vibration at low temperatures which allows the dipoles to orient so much as it is the diminution of the energy factor kT in the Boltzmann distribution expression. Starting at 4.2 °K with boiling point liquid helium we may measure χ on down to 1 °K and in this way establish the curve of Equation (2). The temperature measured from the susceptibility will be called the Curie temperature and denoted by T^*.

But one cannot rely on an extrapolation of such a scale to extremely low temperatures. We have mentioned in earlier paragraphs the existence of forces within the salt which at low temperatures can influence the orientation of the dipoles. This can mean only that at this very low temperature the constant C of Equation (2) will begin to change its value. This breakdown of the validity of the magnetic thermometer is similar to the limitation on the gas thermometer: in the latter the interaction forces cause the gas to condense. Thus the breakdown of the foregoing magnetic method of temperature measurement occurs in just the very region we wish to measure. The difficulty cannot be removed by the choice of a salt whose interaction forces do not set in at these temperatures; indeed, it is only because the interaction forces set in at temperatures below 1 °K that we are able to produce such temperatures. Further, the use of secondary thermometers involves experimental difficulties of temperature equilibrium. Giauque and MacDougall, using magnetically dilute gadolinium phospho-molybdate, have shown that at 0.15 °K the Curie temperature differs by only 0.03 °K. There is little to be gained by using one type of salt as a cooling agent to say 0.1 °K and another, in thermal contact, whose interaction forces set in at 0.01 °K as the thermometer. The intermediate temperature can be obtained with the thermometer salt and lower temperatures are available when needed.

G. The Thermodynamic Temperature Scale Below 1 °K

Giauque and MacDougall, Keesom, Kurti and Simon, de Haas and Wiersma have variously worked out the steps necessary for the establishment of an absolute temperature scale in the new region. The thermodynamic principles are in most cases the same; *i.e.*, $T = \Delta Q/\Delta S$ and the quantities ΔQ and ΔS are experimentally determined. Let us consider the entropy-temperature curve of Fig. 5 to illustrate the required steps. Starting at 1 °K a field, H_1, lowers the entropy by a definite amount (see appendix, this article) while the temperature remains constant because of contact with the liquid helium. Adiabatic demagnetization proceeds to the point, F_1, which has a much lower temperature, T_1, measured on the Curie temperature scale. Letting the salt return to 1 °K, we now begin with a field, H_2, and proceed to the point, F_2, which has a temperature T_2. The curve of S against T^* is thus established. While the values of S are taken from theoretical relationships, the validity of the expression was checked between 4.2 °K and 1 °K where specific heats and temperatures are determined by standard methods. By directly determining the quantity ΔQ released upon magnetization at 1 °K, the entropy drop can be further checked. This can be done by measuring the amount of extra liquid helium boiled away because of the heat ΔQ.

The next step requires the measurement of Q against T^*. Having made a demagnetization to quite low temperatures the procedure calls for pouring in a known amount of heat, ΔQ, while the Curie temperature is continuously determined. Giauque and MacDougall have accomplished this by means of an induction heater made of a gold-silver alloy which is not a superconductor. The amount of heat introduced by such a furnace per second is determined to an unknown constant; this constant is experimentally measured in the region above 1 °K where the Curie temperature and the absolute temperature are identical. A very serious objection to this technique is the fact that only the surface of the salt is heated by the furnace and thermal equilibrium throughout the salt is not established because of the salt's poor conductivity. Kurti, Lainé, and Simon have used another very clever technique; the heating was accomplished by bombarding the salt with γ-rays from a radium salt. Here again the unknown constant is determined by requiring the absolute temperature to be identical with the Curie temperature at 1 °K. Thermal equilibrium is secured by placing the radium symmetrically about the salt.

Q and S having been measured as functions of T^*, the ratio of the slopes of the curves at any point determine the absolute or thermodynamic temperature:

$$T = \Delta Q/\Delta S = (\partial Q/\partial T^*)_{H=0}/(\partial S/\partial T^*)_{H=0}$$

Magnetic fields must be held at zero because both S and Q are functions of the field. The striking results of such measurements are shown in Fig. 7 from the work of Kurti, Lainé, and Simon.

The first departure of T^* from T °K occurs when the crystalline electric field interaction sets in; the second when the magnetic interaction enters. Theoretical treatments by Van Vleck, Hebb and Purcell, and by Debye are in accord with the experimental results.[23, 24, 25]

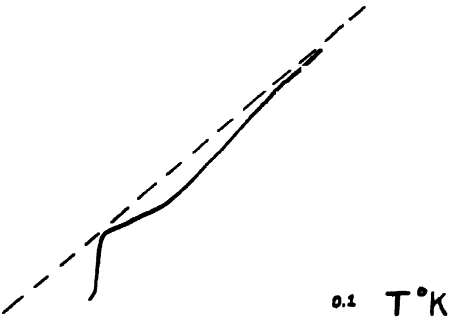

FIG. 7.

Curie temperature, T^*, plotted against absolute temperature T °K.

One should mention the magnetic method of de Haas and Wiersma which tests the ideal behavior of the salt and and sets the limit at which the magnetic thermometer may determine the Thermodynamic Temperature Scale. The ideal behavior does not obtain for zero field, *i.e.*, a field of 100 gauss is needed to make the energy in this field large as compared to the energy of the interaction for cesium titanic alum.

Kurti and Simon have introduced a combination of susceptibility measurements with and without external additional field which determines the absolute temperature. Heating with γ-rays is required and the ideal behavior of the substance is assumed at high temperatures for extrapolation purposes. It was verified that the act of demagnetization was really reversible at these very low temperatures. This method, valid for the entire temperature region, promises to be most useful for future research.

There are of course many interesting features in connection with the physical properties of these salts, and of metals cooled by them, which we cannot discuss in this article. The temperature of a metal, T_m, may be quite different from the temperature of the electron spins, T_s, of the cooling salt owing to poor equilibrium conditions.

H. Toward Absolute Zero

It has been pointed out by Kurti and Simon and by Gorter that still lower temperatures are possible by using substances with nuclear paramagnetism. The interaction energy between nuclear spin and electron spin (hyperfine structure) is so very small that the entropy drop caused by it must occur at extremely low temperatures, *i.e.*, of the order of 1/10,000 °K. Heitler and Teller have indicated that the interaction between crystal lattice and nuclear spin may be so feeble as to give long time effects before equilibrium is established. The experimental procedure will probably consist of a cascade of demagnetizations from an electron spin paramagnetic salt to a nuclear spin one. Thermal contact by liquid helium is possible. The problem of measuring these temperatures will be even more difficult—involving the disturbing of the system by the measuring device similar to the experiments illustrating the uncertainty principle.

I. Appendix:—Dependence of Entropy on a Magnetic Field[23]

At a temperature of 1 °K the N independent paramagnetic ions have a Gibbs free energy, G, expressed by:

$$G = U - TS - H\sigma \tag{3}$$

where σ is the magnetic moment of a single ion. The entropy is calculated from this by:

$$S = -(\partial G/\partial T)_H \tag{4}$$

The free energy is calculated from the statistical expression:

$$G = KT \ln \Sigma\, g_i e^{-\epsilon_i/KT} \tag{5}$$

We now calculate the above expression (5) for Fe-alum. Since kT is greater than the crystalline electric field energy, we have energy states in a magnetic field given by:

$$\epsilon_i = \pm 5\beta H;\ \pm 3\,\beta H;\ \pm \beta H$$

where $\beta = eh/4\pi mc$ is the Bohr magneton.
Substituting, the free energy becomes:

$$G = -KT \ln 2\,[\cosh 5X + \cosh 3X + \cosh X] \tag{6}$$

where $X = \beta H/KT$
We now get from (4)

$$S = K \ln \frac{\sinh 6X}{\sinh X} - KX[6 \coth 6X - \coth X] \tag{7}$$

The same entropy dependence may be calculated from the Langevin-Brillouin expression for the magnetization of a paramagnetic salt. It is to be emphasized that these calculations involve a detailed knowledge of the particular salt used in the experiment.

$$\Delta S = \int_0^{H_1} \left(\frac{\partial M}{\partial T}\right)_H \partial H \tag{8}$$

where M is the magnetic moment calculated by the Brillouin function. See Van Vleck, "Electric and Magnetic Susceptibilities," p. 257, Oxford Univ. Press, 1932.

Acknowledgment

The author is indebted to Professor Simon of Oxford University, with whom he worked, for much of the material presented in this article.[2,3] The establishment of

a thermodynamic temperature scale below 1 °K by Simon, Kurti, Lainé, and Squire will be published shortly and the present article does not include their measurements.

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On the Temperatures of Liquid Helium

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Measurements of the temperatures of liquid helium under various pressures were made recently by Schmidt and one of us.[1] The results were given in the form of differences between the temperatures then measured and those calculated from the vapor pressures according to the formulas which form the basis of "scale 1932." The establishment of a new scale for those temperatures was deferred.

Since then we made a penetrating investigation to see how far the results of those measurements, in connection with other data on liquid and gaseous helium, can be represented by a vapor-pressure formula resting on a sound thermodynamic basis, or two such formulas, one for the He I and the other for the He II range.

II

Introducing for the vapor, the equation of state

$$pv' = RT + B^*p + C^*p^2, \text{ for } T \geq T_1, \tag{1}$$

where the coefficients of p and p^2 are connected with the virial coefficients occurring in the formula

$$pv' = RT\left\{1 + \frac{B}{v'} + \frac{C}{v'^2}\right\}$$

by the relations

$$B^* = B,\ C^* = \frac{C - B^2}{RT}, \tag{2}$$

one derives by means of the Clapeyron-Clausius equation †

$$^{10}\log p_{cm} = \frac{5}{2}\,{}^{10}\log T - 4.1249 + 0.43429\left\{-\frac{k_1}{T} + l_1 - P_T\right.$$

$$\left.\int_{T_1}^{T} \frac{r_T}{RT^2}dT - \frac{1}{RT}[(B^* - v_1'') + \tfrac{1}{2}C^*(p + p_1)](p_{atm} - p_{1atm})\right. \tag{3}$$

In this formula

$$P_T = \int_{T_1}^{T}\frac{dT}{RT^2}\int_{T_1}^{T} c''dT, \tag{4a}$$

$$r_T = (v'' - v_1'')T\frac{dp}{dT} - \int_{T_1}^{T}(v'' - v_1'')\frac{dp}{dT}dT. \tag{4b}$$

---

† Bleaney and Simon[8] are not right in supposing that there is an error in the coefficient of log T in the formula given in 1932 for the vapor pressures of He II. This coefficient and that of $1/T$ were calculated so as to give the closest agreement with the experimental data existing then. *Cf.* IV as to an empirical formula for P_T, valid for the He I temperatures.

The suffix $_1$ always refers to the saturated vapor or liquid condition at the temperature T_1. We chose as T_1 the lowest temperature at which the specific heat c'' had been measured by Miss Keesom and one of us.[2] The saturated vapor is indicated by ′, the liquid under its saturated vapor pressure by ″.

k_1 and l_1 are constants determined by

$$k_1 = \frac{W_1' - W_1'' - 5/2RT_1}{R}, \tag{5a}$$

$$l_1 = \ln p_1 + \frac{W_1' - W_1'' - 5/2RT_1}{RT_1} - \frac{5}{2}\ln T_1, \tag{5b}$$

where W means the enthalpy. T_1 is supposed to be still high enough to be sure that $c'_{p_1} = 5/2R$.

III

In applying Equation (3) to helium, our first aim was, after having determined the constants k_1 and l_1 from values of the vapor pressure at suitable temperatures, to derive values of B^* for the temperatures below the λ point. As a matter of fact, if we accept that for these temperatures the term with C^* can be neglected, B^* is then the only quantity in Equation (3) that is not known from experimental data.[†] For these temperatures the term depending on r_T can be neglected. T_1 was chosen 1.235 °K, $p_1 = 0.088$ cm mercury.

It appeared that the term $\frac{B^* - v_1''}{RT}(p - p_1)$ calculated in this way from the experimental vapor pressures did not approach 0 for $p \rightarrow p_1$, as it necessarily must do. After checking different suppositions we came to the conclusion that the vapor pressures given in Communication No. 250c for temperatures below the λ point must be somewhat in error.

In adopting a plausible course of the term mentioned above as a function of T, we calculated that the temperatures below 1.5 °K probably are in error, to an estimated amount of 0.008 degree at 1.3 °K, in the sense that the temperature is really higher than corresponds to the vapor pressure measured in 1937. Above 1.5 °K deviations seem to be smaller than 0.001 degree.

It is satisfying to see that these conclusions agree with the results of Bleaney and Simon[3] recently derived by quite another series of considerations, based on substantially the same experimental data.

As, however, our estimations were based on a rather arbitrary interpolation, we then initiated experiments to check them, by directly comparing the vapor pressures measured in the vapor-pressure apparatus of Communication No. 250c with those measured in vapor-pressure tubes designed in such a way as to avoid the influence of a film of He II creeping up, as well as with the pressure above the liquid of the cryostat bath.

These experiments have not yet been completed. Our first results are that differences occur between the pressures measured on these different ways, and that these differences are dependent on peculiarities of the experiment, such as the difference in level between the cryostat bath and the liquid within the vapor-pressure tube. These pressure differences amount to, *e.g.*, some tenths of a mm of mercury, even above 1.5 °K, and may be decidedly larger than those corresponding to the differences in temperature mentioned above. So we must postpone to a later paper a definite assertion with respect to a more exact relation between vapor pressure and temperature in the He II range.

[†] We intentionally did not introduce the chemical constant, to be independent from specific heats of the liquid at lower temperatures.

IV

Meanwhile one of us[4] has calculated a pair of interpolation formulas for the He I range. They are valid from 2.19 to 4.20 °K:

$$ {}^{10}\log p_{cm} = -\frac{4.7921}{T} + 0.00783T + 0.017601T^2 + 2.6730 \qquad (6a) $$

and

$$ {}^{10}\log p_{cm} = \frac{-4.7948}{T} + 0.0343\ {}^{10}\log T + 0.018024T^3 + 2.6775 \qquad (6b) $$

Both formulas agree within about 0.001 degree with the experimental data of 1937.

We remark that for the quantities mentioned in Equations (4a) and (4b) the following empirical formulas hold for $2.19 < T < 4.20$:

$$ P_T = 0.9191\ {}^{10}\log T + 0.1442\ T - 0.5176 $$

$$ \int_{T_1}^{T} \frac{r_T}{RT^2}\, dT = 37 \times 10^{T-8} $$

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Thermal Equilibrium at Temperatures Below 1 °K

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Investigations at temperatures below 1 °K, obtained by demagnetization of a paramagnetic salt, may be divided into two groups; one may either study the magnetic properties of the salt itself or try to investigate the properties of other substances cooled by contact with the salt.

It is only natural that up to the present more attention has been given to the first group of investigations; a knowledge of the magnetic properties of a salt is essential if it is to be used at full profit for cooling purposes. The ultimate goal of this research must be to find the magnetic moment, entropy and interior energy as a function of the magnetic field (H) and the absolute temperature (T), and to compare these data with theory. Considerable progress has been made in this direction.

The object of the present paper is to consider in more detail some of the difficulties connected with experiments of the second group.

II

It is well known that the cooling power of a paramagnetic salt is more than sufficient for cooling other substances. The only substance with a specific heat of the same order of magnitude as a paramagnetic salt in a magnetic field is liquid helium, but even in this case 1 cc of iron ammonium alum is sufficient to cool about 1 cc of liquid helium to a temperature well below 1 °K. Also the time available for experiments is sufficiently long; even leads for resistance thermometers or heating coils do not give rise to a disturbingly quick warming rate. Besides technical difficulties, the main problem is whether a piece of matter will really assume the temperature derived from the magnetic properties of the salt.

III

It is imaginable that near the absolute zero no temperature can be defined. The number of degrees of freedom which is not frozen in decreases rapidly with decreasing temperature, and it may become so small that no consistent application of statistical mechanics is possible. Another possibility is that the time necessary for establishing thermal equilibrium becomes extremely long. However, there is at present no evidence of such a breakdown of thermodynamics for the "spin system" (the system of magnetic ions), the properties of which alone determine the magnetic behavior. So we shall assume that there exists always a spin temperature T_s. Only in very rapidly changing fields the spin system might pass through states of non-equilibrium.

We shall assume that there exists also a lattice temperature T_l. It is not evident that this is true if we disregard the trivial—but from an experimental point of view quite serious—difficulty which may arise because of the very low thermal conductivity of compressed powders, such as those used by Kürti, Simon and others. Also, in the case of a solid block of salt, it might be doubted whether thermal equilibrium between the heat waves—which at very low temperatures will be almost macroscopic wave-length—will be established within a reasonable time. This question, which is intimately connected with the problem of heat conduction, is one of many interesting topics in this new field of research. Here we shall only point out that it may lead to additional complications not considered in the following.

IV

It is problematic whether a sample of matter can be connected in such a way to the salt that its temperature T_m is equal to T_l. We shall first leave aside this point and discuss the question whether $T_s = T_l$.

Let us suppose that by some exterior influence we have been able to create a difference between T_s and T_l. Then heat exchange will take place between spin and lattice. For the amount of heat (in ergs) exchanged per second for one gram of the substance we write

$$dQ = f(H, T_s, T_l)$$

If C_l is the specific heat of the lattice, and C_s the specific heat of the spin system, it follows that for an adiabatically insulated salt we have[1,2]

$$\frac{dT_s}{dt} = -f(H, T_s, T_l)/C_s \tag{a}$$

$$\frac{dT_l}{dt} = +f(H, T_s, T_l)/C_l \tag{b}$$

For small values of $T_s - T_l$ we may also write

$$dQ = \alpha_H(T_s - T_l)$$

where

$$\alpha_H = \left[\frac{\partial f(H, T_s, T_l)}{\partial T_s}\right]_{T_s = T_l}$$

Since C_l is very much smaller than C_s the time in which $T_s - T_l$ decreases by a $1/e$ will be given by

$$\tau = C_l/\alpha_H$$

However, even in the best experimental arrangement insulation will not be perfect; there will always be a heat flow, F, coming to the lattice, and this will lead to a temperature difference

$$\Delta T = F/\alpha_H \tag{c}$$

If for a salt at 0.05 it is possible to keep ΔT below 0.005, it follows that

$$\alpha_H > \frac{F}{0.005}$$

and hence

$$\tau < \frac{C_l}{F} . 0.005$$

this will usually be very short; even in the best arrangement possible a crystal lattice not coupled to a spin system would rise very rapidly in temperature. For iron ammonium alum at 0.05 °K, C_l is roughly 0.01 erg/degree gram[3], and hence even for an F value as low as 5×10^{-5} erg/gr sec (which is much lower than the lowest value ever obtained in actual experiments) τ would be only 1 second. We conclude that the question whether in practice $T_s = T_l$ is determined by condition

(c) : the exchange of energy between spin and lattice has to be sufficient to counteract the inflow of heat, in which case it will be amply sufficient to cool the lattice in a very short time.

V

It is fortunate that in the liquid helium range fairly reliable data on α_H are available. De Haas and du Pré[4] have measured the alternating part of the magnetic moment of a salt when it is subjected to a constant field and a (much smaller) alternating field in the same direction. The measurements are an extension of the work of Gorter and his collaborators on paramagnetic relaxation. Now Casimir and du Pré[1] were able to show that the results of such experiments can be explained in a very simple and satisfactory way if we assume that there exists always a spin temperature, T_s, which may be different from the lattice temperature, T_l (which itself is equal to the temperature of the helium bath). In the limit of high frequencies the coupling between spin and lattice does not lead to an appreciable loss of energy during one cycle, and the spin system behaves as if it were adiabatically insulated. For low frequencies, on the other hand, T_s is always equal to T_l. The results show that the assumption of spin equilibrium is justified even in alternating fields. They enable us to find α_H and incidentally they provide us with a rather efficient method for determining the specific heat of the spin system.

For iron ammonium alum in a zero external field, α_H is of the order of 10^5 ergs/sec degree gram, and it does not vary appreciably with temperature. If it is permissible to extrapolate this result, we can conclude that the rate of exchange of energy between spin and lattice is always amply sufficient, not only for cooling the lattice in a finite time when thermal insulation is perfect, but also for keeping $T_s - T_l$ very small under ordinary working conditions. However, no satisfactory theoretical explanation has been given for the values of α_H found by de Haas and du Pré; calculations of Heitler and Teller[5] lead to much lower values. Hence there is no theoretical argument on which an extrapolation can be based.

VI

The experimental study of temperature quilibrium is complicated by the circumstance that it is impossible to determine the temperature of the lattice unless we add a third body, for instance a resistance thermometer. And we do not know whether the temperature of this thermometer, T_m, will be equal to T_l. Besides the heatflow to the lattice, F, there will also be an amount of heat, F', developed in or leaking to the thermometer. The energy exchange, α_H, must be sufficient to counteract $F+F'$, the exchange between lattice and thermometer sufficient to counteract F'. If a difference $T_m - T_s$ is found, we do not know whether this is due to a difference $T_m - T_l$, $T_l - T_s$, or to both.

It is not easy to find a simple and conclusive criterion for the equality of T_m and T_s, although it is often easy to show that there is no equilibrium. The first question is whether the resistance, R_m, of the thermometer is a continuous and unique function of T_s. If for the same T_s we find different values of R_m, there is certainly no equilibrium. But the opposite is not true: if F and F' are reproducible functions of the temperatures, R_m will always depend in a continuous way on T_s. The method used by Allen and Shire[6] is open to the same criticism.

A much stronger case for thermal equilibrium can be made out if R_m does not change when F' is changed (which may be done by changing the measuring current). Of course it is not unimaginable that the function $f\ (T_s, T_l)$ is zero for $T_s - T_l < 0.01$ °K say, and very large for larger differences; but such behavior is highly improbable.

Zweers and I have tried to apply this method in some preliminary experiments on gold and phosphor bronze wires. These wires were stuck by means of Bakelite varnish on a spheroid ground from a large block of iron ammonium alum. It seems reasonably safe to assume that the temperature distribution inside the crystal was homogeneous. Down to 0.3 °K all went well. Increasing the measuring current had a slight effect, but extrapolation to $F'=0$ was easily possible, and F was much smaller than the largest F' values. At lower temperatures, however, no unique extrapolation could be made and the wires certainly did not reach the lowest spin temperature, T_s, which was of the order of 0.05 °K. We are inclined to believe that this failure is due to lack of equilibrium between lattice and wires rather than to a difference between T_s and T_l, but of course this has not been proved.

VII

The most promising method of obtaining a satisfactory heat contact between lattice and thermometer and at the same time of insuring a homogeneous temperature distribution even in a powder seems to be the use of a salt immersed in liquid helium. Kürti and Simon succeeded in doing this by using a salt in a metal container, filled with a hundred atmospheres of helium at room temperature. But this method has certain disadvantages: it is almost impossible to put a thermometer wire into the helium, and without such an arrangement it is very difficult to prove that there is temperature equilibrium. It is to be hoped that another solution to this problem will be found. Only when it has been established that the heat exchange between helium and salt is very efficient—and we have little doubt that this will be the case—will it be possible to obtain more definite information on the exchange of energy between spin and lattice.

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The Field of Extreme Temperatures

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Introduction

An ever-increasing amount of scientific and industrial work at very high temperatures is being performed in such diverse fields as spectroscopy, metallurgy, the manufacturing of refractories and parts of radio tubes, the determination of melting points and phase equilibria, welding and geophysics. The materials available for work at extreme temperatures are briefly surveyed in the first part of this paper and the methods of producing very high temperatures in the second part. Since it is impossible to cover the entire field in a brief contribution, a bibliography is included, containing some references for further information. Stellar temperatures are not discussed here, since they are treated in the contribution by G. P. Kuiper in Chapter IV.

I. Materials

Desirable properties of materials to be used at high temperatures are strength, resistance to mechanical and chemical corrosion, and stability in oxidizing, neutral and reducing atmospheres, or in a vacuum.

Table 1. Melting Point of Some Minerals and Ceramic Products.

Material	Melting Point (°C)	Material	Melting Point (°C)
Alumina brick	1750–2050	Mullite	1827
Bauxite brick	1730–1850	Porcelain, technical	1670–1920
Carbon brick	> 2000	Silica brick	1700–1750
Chrome brick	1950–2200	Spinel	2135
Fireclay brick	1580–1880	Zircon brick	2200–2700
Magnesite brick	2200		

Table 2. Melting Point of Some Elements.

Symbol	Element	Melting Point (°C)	Symbol	Element	Melting Point (°C)
Be	Beryllium	1280 ± 5	Pd	Palladium	1554 ± 1
B	Boron	2300 ± 300	Pt	Platinum	1773.5 ± 1
C	Carbon	3700 ± 100*	Rh	Rhodium	1966 ± 3
Cr	Chromium	1800 ± 50	Ru	Ruthenium	2500 ± 100
Co	Cobalt	1490 ± 20	Si	Silicon	1430 ± 20
Au	Gold	1063.0 ± 0.0	Ta	Tantalum	3000 ± 100
Hf	Hafnium	2227	Th	Thorium	1800 ± 100
Ir	Iridium	2454 ± 3	Ti	Titanium	1820 ± 100
Fe(δ)	Iron	1535 ± 3	W	Tungsten	3410 ± 20*
Mn	Manganese	1260 ± 10	V	Vanadium	1735 ± 50
Mo	Molybdenum	2625 ± 50*	Zr	Zirconium	1857
Ni	Nickel	1455 ± 1			

*To be heated at high temperature in a reducing or neutral atmosphere, or in a vacuum.

Melting points of some products of the ceramic industry and of some minerals are given in Table 1. It will be seen that the usefulness of most materials does not continue beyond 1700 °C; however, some "special refractories" may be used at temperatures in excess of 2000 °C. Improvements in usefulness of ceramic products have been accomplished by fusing the material and casting it into the desired shape, *e. g.*, refractories for glass tanks.

Tables 2, 3 and 4 have been compiled of elements, oxides, carbides, nitrides and borides which are being used in work at high temperatures, now that difficulties in manufacturing articles from pure elements, oxides, etc. are being overcome. Excellent "super-refractories" are produced by *sintering* Al_2O_3, BeO, CeO, ThO_2, ZrO_2, etc., at temperatures of 1900 °C, or higher. Others are being manufactured from *pre-fused* Al_2O_3, MgO, ThO_2 and ZrO_2, with or without a ceramic bond. Fused alumina and magnesia are being used for many purposes in both laboratory and industry, whereas thoria and zirconia are mostly used in the laboratory.

Table 3. Melting Point of Some Oxides.

Material	Melting Point (°C)	Material	Melting Point (°C)
Al_2O_3	2050	Mn_3O_4	1560
BeO	2530 ± 30	NiO	1990
CaO	2585	SiO_2 (Cristobalite)	1729
CeO	>2600	ThO_2	3050 ± 25
Ce_2O_3	1965	SnO_2	1850 ± 50
Cr_2O_3	2275 ± 25	TiO_2	1560
CoO	1810	WO_2	1575 ± 25
HfO_2	2774 ± 25	V_2O_3	2240
FeO	1380 ± 5	Y_2O_3	>2400
Fe_2O_3	1570 ± 20	ZnO	1975 ± 25
MgO	2800	ZrO_2	2715 ± 20
MnO	1785		

Table 4. Melting Point of Some Carbides, Nitrides, and Borides.

Material	Melting Point (°C)	Material	Melting Point (°C)
B_4C	2350	TiC	3137 ± 90
CaC_2	2297	WC	2867 ± 50
HfC	3887 ± 150	W_2C	2857 ± 50
MoC	2692 ± 50	VC	2827
Mo_2C	2687 ± 50	ZrC	3532 ± 125
SiC	2537	4TaC + 1ZrC	3932
TaC	3877 ± 150	4TaC + 1HfC	3942
ThC_2	2773		
AlN	2200	SiN	1900
Be_3N_2	2200	TaN	3087 ± 50
BN	3000	TiN	2947 ± 50
CaN_2	1195 ± 1	VN	2050
HfN	3307	ZrN	2982 ± 50
HfB	3062 ± 50	ZrB	2992 ± 50
WB	2922		

The super-refractories show low permeability at high temperatures, great strength and good resistance to corrosion. The thermal expansion of CeO, MgO and ZrO_2 is rather small, resulting in good spalling resistance (ability to withstand sudden changes of temperature). Some materials of Tables 2 to 4 must be heated in a neutral or reducing atmosphere or in a vacuum as noted. Nearly all metals of Table 2 will be attacked at high temperatures by silicon, phosphorus and carbon if heated in a reducing atmosphere. Platinum should not be heated in a reducing atmosphere in the presence of metallic vapors.

II. Methods of Producing Extreme Temperatures

Some methods of producing extreme temperatures, unlike those for producing moderately high temperatures, are available only for very short periods of time. In this chapter, we discuss separately the more important methods of producing extreme temperatures for long and short periods of time. A few characteristic examples of furnaces are presented.

A. Long Periods of Time. Important considerations in this type of work are the control of the speed of heating; the production of oxidizing, neutral or reducing atmospheres in the furnace; the presence of a zone of uniform temperature large enough to carry out the work contemplated; and the possibility of accurate measurement of the temperature. Additional considerations will be added, from case to case. Furnaces may be heated by solid, liquid and gaseous fuels, by electric energy, or by radiant energy from the sun.

1. Furnaces for Solid, Liquid and Gaseous Fuels. Many furnaces of this type have been built for high-temperature work in the laboratory and in industry. Furnaces fired with powdered coal are used up to 1800 °C, the temperature being limited by the refractory materials used in construction. Temperatures around 3000 °C may be obtained by the oxidation of metals, *e. g.*, thermite (containing aluminum and iron oxide). Liquid fuels have been used, in connection with oxygen, for work up to 2600 °C. Many types of gas-fired furnaces have been built for work at high temperatures. More than 3000 °C may be obtained by the use of acetylene-oxygen.

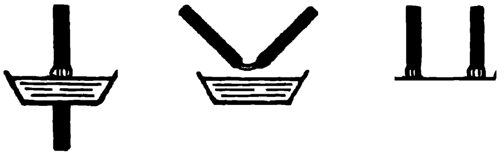

Fig. 1. Electric arc furnaces. (a) direct heating; (b) indirect heating; (c) combination heating.

Most furnaces using solid, liquid and gaseous fuels may be easily adjusted to maintain a given temperature for a long period of time; the atmosphere may be readily changed from oxidizing to neutral to reducing.

Because of the limitations in refractories, the region of maximum temperature is often removed from the walls of the furnace for the protection of the furnace lining. Such concentration of heat, *e. g.* along the axis of the furnace chamber, is accomplished by the arrangement of several burners under various angles. The material to be heated is brought from above or below into the zone of maximum temperature.

2. Electric Furnaces. *a. Electric Arc.* The temperature of the electric arc varies from 3400 to 4900 °C, depending on current density, atmospheric pressure, and the kind of electrode—carbonic, metallic, or compound. Even higher temperatures may be obtained by operating at high pressure. Temperatures up to 3000 °C may be easily maintained in an industrial furnace by the use of one or several arcs. The atmosphere may be varied from oxidizing to reducing.

Industrial and laboratory furnaces make use of the electric arc between carbon and graphite electrodes, or of the arc between an electrode and the material to be heated. We also find the electric arc used in combination with gas, oil or powdered coal burners, or with resistance heating. A few examples of arc furnaces are presented schematically in Fig. 1, showing direct heating, indirect heating, and a combination of arc and resistance heating (arcs at electrodes, resistance heating between arcs).

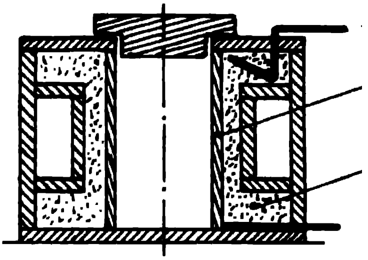

FIG. 2.
Furnace with granulated resistor. (a) granulated carbon; (b) refractory tube.

Other applications of the heat from the electric arc are (1) the welding of steel plates, etc., in which the arc is excited between a metallic or carbonic electrode and the pieces to be welded; and (2) the use of various types of arc furnaces in the fixation of atmospheric nitrogen, forming nitric oxide, which is converted into nitric acid and other products.

b. Direct Heating. Furnaces with heating elements of granulated carbon or graphite form a connecting link between the arc and the method of direct heating, because of the occasional formation of small arcs between individual grains of the resistor. Fig. 2 presents schematically a laboratory test kiln of this type. The material to be treated may be placed on either the outside or inside of a powdered resistor which is directly heated. Installations of this type are available in large industrial kilns, *e. g.*, those manufacturing silicon carbide and graphite at temperatures from 1500 to 2500 °C.

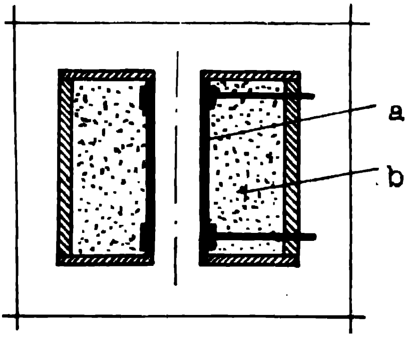

FIG. 3.
Carbon tube furnace. (a) carbon tube; (b) heat-insulating material.

Direct heating of the charge is carried out in furnaces similar to the arc furnace of Fig. 1, c, but with electrodes inserted into the material to be heated. In many fields, furnaces of this type are being used for large-scale production.

c. Furnaces with Resistors in the Form of Tubes or Rods. Fig. 3 presents an electric furnace with a carbon tube which is heated to a high temperature, and within which is placed the material to be heat-treated. Tubular heating elements are manufactured from carbon, graphite, silicon carbide ("Globar" or "Silit"), tungsten, molybdenum, and, in a few cases, iridium. The atmosphere of these kilns varies, depending upon the type of heating unit used. Furnaces for spectrographic work in the vacuum have been perfected by King, Freundlich and others.

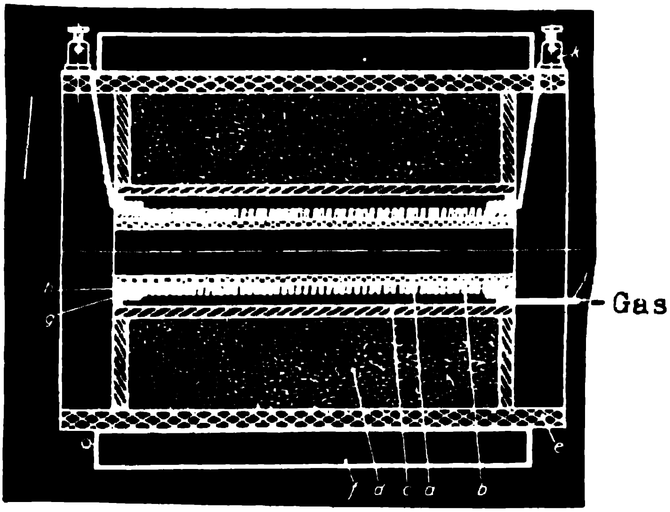

FIG. 4. Wire-wound furnace with external winding. (a, c) sintered refractory tubes; (b) heating coil (tungsten); (e, h) refractories; (d) pulverized zirconia; (f) water jacket; (g) tungsten ribbon; (i) entrance of protective gas; (k) binding post. [Cohn, W. M., *Z. techn. Physik*, 9, 114 (1928).]

Many types of kilns are available for laboratory and industrial work which use heating elements of silicon carbide in the shape of rods. Kilns of this type may be operated continuously up to 1500 °C, and for short periods of time at higher temperatures.

If the article to be heat-treated is in the shape of a metallic rod, wire, or tape, *e. g.*, tungsten, it may be directly heated by passing the electric current through it. The wire may be processed either in a periodic kiln or in a continuously working installation.

d. Wire and Ribbon-wound Furnaces. A furnace of this type is shown in Fig. 4. The heating chamber may be equipped with internal or external windings in the shape of a spiral, or, according to Navias, in the shape of zigzag windings. A wide variety of resistance wires and ribbons, *e. g.*, nickel-chromium alloys, is available up to 1100 °C. Higher temperatures are obtained by the use of nickel, iron, platinum and platinum alloys. For temperatures above 1500 °C, molybdenum, tungsten and rhodium are used.

Heating of molybdenum and tungsten must be carried out in a reducing or neutral atmosphere or in a vacuum. If the material to be heated in such a furnace must be kept in an oxidizing atmosphere, it is necessary to place the winding on a gas-tight tube or muffle, *e.g.*, fused alumina, thereby permitting an oxidizing atmosphere inside the furnace and keeping the heating element in a reducing or neutral atmosphere (see Fig. 4).

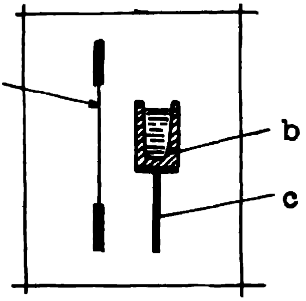

FIG. 5.

Electron-bombardment furnace. (a) incandescent wire, cathode; (b) container with sample, anode; (c) support of anode.

e. Induction and High-frequency Furnaces. An induction furnace is built similar to a transformer, the material to be heated forming the secondary winding of the transformer (if the material is non-conducting at the start of operation auxiliary coils are inserted). Temperatures are limited by the refractories in contact with the material to be heated.

In high-frequency furnaces the energy is transferred by induction from a winding to the charge. Since the charge is separated from the coil which serves to transfer the electric energy, the temperature is limited only by the material to be heated. Furnaces of this type have been built for temperatures in excess of 3000 °C, for use both in the laboratory and in industrial installations. Frequencies range from 20,000 to 50 periods depending on the size of the furnace. Heating may be carried out in an oxidizing, neutral, and reducing atmosphere, or in a vacuum.

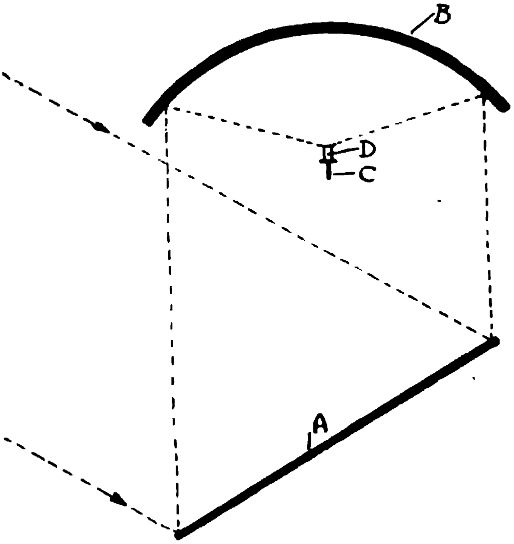

FIG. 6.

Sun furnace. (A) plane mirror; (B) 100-in. Straubel mirror; (C) support of sample; (D) sample. [Cohn, W. M., *Trans. Electrochem. Soc.*, **68**, 69 (1935).]

f. Electron Bombardment. Fig. 5 presents schematically a furnace for heating a conducting sample by electron bombardment. Electrons from hot or cold cathodes may be used for heating the sample which forms the anode. Since the source of electrons is not in direct contact with the anode, extreme temperatures may be obtained, limited only by the melting or vaporization of the material heated. A more general application of this type of heating encounters some difficulty, because it must be carried out in a vacuum.

3. Solar Furnaces. The radiant energy from the sun has been used for producing extremely high temperatures. Fig. 6 presents schematically the sun furnace developed by R. Straubel of the Zeiss Works in Jena. The radiation is concentrated in the sample by means of a heliostat and a 100-in. searchlight mirror; since the focus is of only $\frac{5}{16}$ in. in diameter, temperatures in excess of 3000 °C may be produced in it. Another type of sun furnace for high temperature has been designed by Dr. G. E. Hale of the Mount Wilson Observatory, Pasadena. A number of lenses are used to concentrate the energy in the common focus, containing the material to be heated.

The solar furnace has several advantages over other furnaces: heating is done under very pure conditions, and in an oxidizing atmosphere; no electric or magnetic fields are present which may disturb the reactions or spectra to be studied; a very short time is required for obtaining high temperatures, *e. g.*, more than 3000 °C may be reached in about 30 seconds. By placing a quartz-glass container over the sample, it is possible to work in a reducing or neutral atmosphere, or in a vacuum.

B. Short Periods of Time

The following methods of producing extreme temperatures are available only for short periods of time. A very high temperature is generated if the front of a shock wave, accompanying the detonation of a solid or gaseous explosive, meets an obstacle such as a solid wall, or if the wave fronts from two explosives meet each other. No exact measurement of the temperature generated has been possible. However, the spectrum of the light emitted is that of a blackbody at a very high temperature; superimposed is a continuous spectrum of luminescent radiation, which seems to be due to continuous electron radiation. Similar phenomena are observed upon discharging a rifle into a closed container, such as another rifle. Then, theoretically, temperatures as high as 8000 °K are expected.

Very high temperatures are also produced by electrically "exploding" a wire. One or several condensers are discharged through a very thin wire which "explodes" within a very short time. The intensity distribution in the continuous spectrum is similar to the spectrum of the light from the front of the shock wave discussed above. We obtain again the superposition of radiations due to high temperature and luminescence. So far, the temperature of the exploding wire, originally thought to be as high as 20,000 °K, has not been accurately determined.

The methods of obtaining extreme temperatures for brief periods of time have not been used to any great extent in industrial practice. However, the author had an opportunity to apply the method of exploding wires to an industrial problem, analyzing operations which last only a small fraction of a second. It is expected that a more general knowledge of these phenomena will result in their wider application to the problems of industry.

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Chapter 9

General Engineering

Gas-temperature Measurement and the High-Velocity Thermocouple

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Summary

The first part describes the most recent developments, as well as the older methods, of accurately measuring the temperature of gases. None of the apparatus described appeared suitable for use in field investigations wherein it was necessary to measure temperatures of slag-bearing gases up to 3100 °F in pulverized-coal-fired steam boilers.

The second part describes in detail construction and use of a high-velocity thermocouple assembly designed to facilitate obtaining temperature readings and keeping the apparatus in repair even when operating under such adverse conditions as are met with in the furnaces of pulverized-coal-fired boilers.

The theory of the high-velocity thermocouple is simple. An ordinary thermocouple junction inserted in a furnace or duct carrying high-temperature gases under ordinary conditions "sees" walls of different temperature. Where these walls are "cold" boiler tubes for instance, the thermocouple junction, although but a few hundredths of an inch in diameter, will radiate heat to this colder surface and will thus be cooled below the true temperature of the surrounding gas. The resulting error may, at furnace temperature, amount to several hundred degrees.

This difficulty may be overcome to a considerable extent by the use of the high-velocity thermocouple (denoted by HVT) which has a heat-insulating shield, or "radiation-shield," around the tip of the thermocouple junction so that it will be able to "see" only a small portion of the cold walls. A stream of the hot gases is then aspirated past the junction of the thermocouple at high velocity. This increases the heat transfer by convection from the gas to the thermocouple tip, thereby causing the reading to approach the true gas temperature.

The third part presents some empirical data to indicate the magnitude of the temperature-measuring errors that may be expected in steam-boiler practice and in equipment operating under similar conditions.

I. Methods of Gas-temperature Measurement

Errors in Gas-temperature Measurement

In industrial application, thermocouples are perhaps more used than any other type of gas temperature-measuring device for the higher temperatures. For that reason this discussion of the errors involved in gas-temperature measurement will refer specifically to thermocouples. However, as the following will indicate, the causes which result in thermocouple error also result in errors with other temperature-measuring devices.

The measurement of the temperature of a gas is subject to errors which do not occur in the case of a solid or liquid. A thermocouple of sufficient length or ordinary design, used with a good indicating instrument, when immersed in a hot liquid, will give the temperature very accurately. Similarly, a thermocouple peened into a surface will also give an accurate reading, if certain ordinary precautions are observed. As no heat is lost by the thermocouple it must reach the temperature of the material very rapidly.

On the other hand a different condition exists for a gas. A thermocouple immersed in a gas receives heat by convection from the gas, but there will also be radiant-heat exchange with the chamber walls which it can "see." If the wall surfaces "seen" are at the same temperature as the gas, the thermocouple will read the true temperature of the gas, because no radiant-heat exchange will take place. On the other hand, if the containing walls are hotter than the gas they will radiate heat to the thermocouple which, because of the extra heat received, will read higher than the true gas temperature. If the walls are at a lower temperature they will absorb radiant heat from the thermocouple and hence the thermocouple will read lower than the true gas temperature. A most important case is that of a modern steam-boiler furnace where the combustion gases are often completely surrounded by "cold" water-wall surface.

The hourly radiant-heat exchange from the thermocouple to the surrounding surfaces is given by Equation (1) (the Stefan-Boltzmann law), and the hourly convection heat from the gas to the couple by Equation (2):

$$Q = CeA_1\left[\left(\frac{T_t}{100}\right)^4 - \left(\frac{T_w}{100}\right)^4\right] \tag{1}$$

$$Q = h_cA_2(T_g - T_t) \tag{2}$$

where Q = hourly heat transferred (Btu/hr);
A_1 = area of the thermocouple surface (ft^2);
A_2 = area of the gas film around the thermocouple (ft^2);
C = the coefficient of a blackbody (0.1723);
e = the emissivity of the thermocouple surface;
h_c = coefficient of convection heat transfer (Btu/ft^{2}hr °F);
T_t = temperature of the thermocouple (°R*);
T_g = temperature of the gas (°R);
T_w = temperature of the walls (°R).

The heat received (or lost) by the thermocouple by convection is equal to the heat lost (or gained) from the thermocouple by radiation at its equilibrium temperature, Equation (3).

$$CeA_1(T_t^4 - T_w^4) = h_cA_2(T_g - T_t) \times 10^8 \tag{3}$$

Since radiation is proportional to the fourth power of the absolute temperature, the radiant-heat transfer will be very great at high temperatures where the wall temperature is at all different from the gas temperature. A thermocouple in a gas at 2500 °F located within walls at 2300 °F will have a much greater relative error than a gas at 700 °F located in a flue at 500 °F for the same temperature difference of 200 °F. Where the thermocouple is located in gases at say 2000 °F adjacent to cold boiler tubes at 350 °F, the measurement may be very much in error.

The presence of radiating gases and glowing carbon particles, as in pulverized-fuel firing, complicates mathematical consideration, since these substances will also radiate to the thermocouple to an extent governed by their volume and their concentration, among other things. The presence of these heat radiators which are also absorbers, will, however, ordinarily decrease the indicated error.

The foregoing explanation is perhaps unnecessary as this error has been rather well known and extensively pointed out in the literature.[20,21,22,26,53B,53C,94,104,110] It has been especially treated by Kreisinger and Barkley,[1] but it is only recently that it has been sufficiently recognized as a source of inaccuracy. Quite often the gas temperatures indicated by ordinary thermocouples located among the relatively cold tubes in the various passes of a steam boiler are carefully recorded to the last degree when errors of as much as 500 °F may readily exist.

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* °R (Rankine) = °F + 459.7°.

Although the preceding discussion refers to thermocouples in boiler gases, the relations hold for all cases involving a gas in which there is a thermometer, thermocouple, or similar means of measurement of its temperature.

Methods of Eliminating Error

There have been many means advanced for determining gas temperatures. Twenty-six of these will be briefly described.

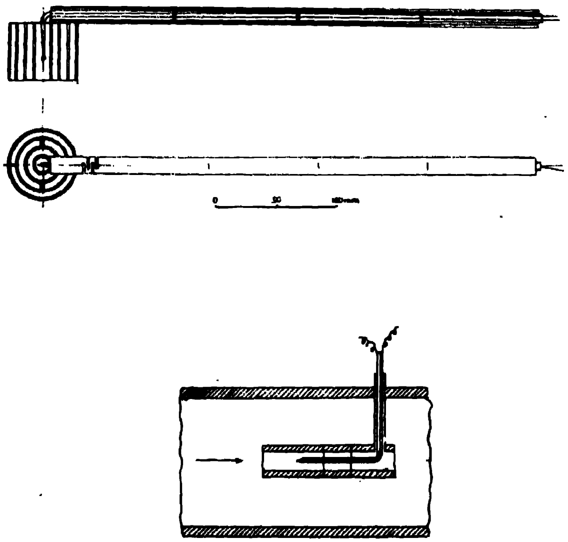

FIG. 1. Two kinds of thermocouple shields. Top: composite type of four separate shields used by Lindmark in a large duct. Bottom: a less accurate "tomato-can" type of shield suggested by a test code.

1. **Covering of Low Emissivity.** It is possible to cover the sensitive element (hot junction of a thermocouple or bulb of a thermometer), with a material having a low emissivity, which, while not affecting the convection heat transfer from the gas to the sensitive element, does however decrease the radiation to other surfaces. W. C. Wells[27] compared the readings in the atmosphere of a bare thermocouple and one covered with gilt paper, finding a difference of about 8 °F. Mottleson[24] suspended a bare thermometer and one covered with a polished silver shield in the air above a red-hot furnace. The average reading of the silver-shielded thermometer was 320 °F, while the reading of the bare thermometer was 502 °F. It is impractical to use this method at high temperatures in corrosive and dust- or slag-carrying gases.

2. **Radiation Protecting Shield.** Shields may be placed around the thermocouple hot junction or thermometer bulb so that it cannot "see" the colder sur-

faces, as in Fig. 1. In this case the shield (or shields) assumes a temperature between that of the thermocouple and the cold walls. This decreases the radiation error,[26,28,29,31,32,33,34,95] but unless the gas flows through this shield with an appreciable velocity, a considerable error still exists. The difficulty of assuring adequate gas flow renders this method of little value except in special cases, such as in a pre-heated air duct under pressure, Fig. 12.

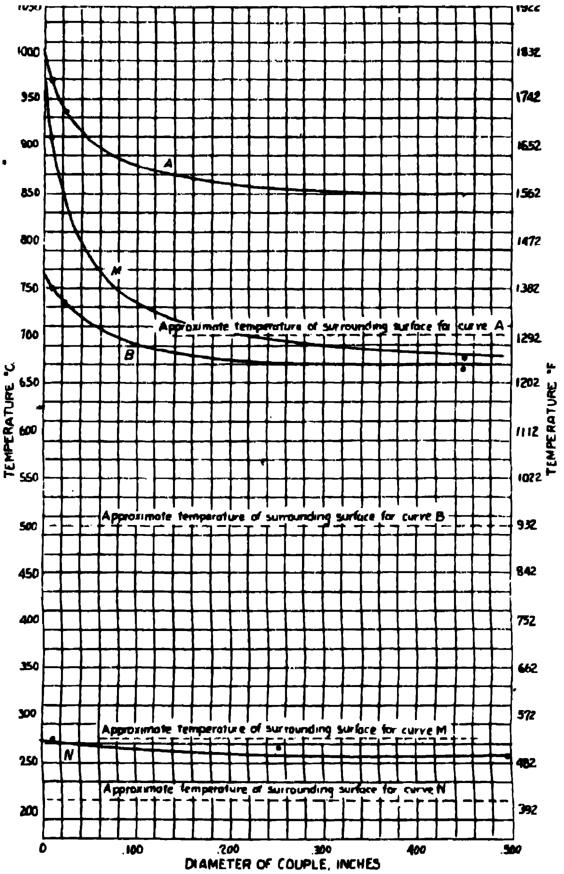

FIG. 2. Relation between diameter of thermocouple and temperature indicated by thermocouple when measuring temperature of hot gases surrounded by cooler surfaces (Kreisinger and Barkley).

3. **Small-diameter Thermocouple.** The radiation error of a thermocouple wire decreases as the size of the wire is decreased, because of the existence of a gas film. Because of this film the area receiving convection heat from the gas is larger than the area (actual surface) of the thermocouple which is radiating through the surface film. An excellent discussion of this has been given by the Bureau of Mines.[1] On this basis a wire of zero diameter would give the true gas temperature. As very small wires are too fragile for practical use, this method is merely an approach toward the solution.

4. **Number of Thermocouples of Different Sizes.** As noted in the previous method, the accuracy of a thermocouple increases with a decrease in diameter. Plotting readings from a number of adjacent ordinary thermocouples of different sizes and extrapolating to a zero diameter thermocouple, the true gas temperature, that is, the temperature that a thermocouple of zero diameter would give, can be obtained. This method has been used by a number of investigators.[1, 12, 14, 26, 30, 53D 53K, 53M, 55, 56, 57] An example of the results obtained by Kreisinger and Barkeley[1] is shown in Fig. 2.

5. **Use of Heated Wires of Different Sizes.** A variation of the foregoing method has been described by Pfriem,[98] who developed a method by which temperatures can be derived either from observations made with two resistance thermometers of different diameter wire carrying the same current, or with two identical thermometers carrying different currents.

6. **Two Thermometers with Different Emissivities.** This method was proposed by Robinson.[2] If the bulbs of two identical thermometers are covered by two materials of different emissivities, it is possible to set up an equation involving the temperature readings of the two thermometers and the emissivities of their coverings. In dust- or slag-laden and corrosive gases this method is of little value.

7. **Bare Thermocouple with Calculated Correction.** In Equation (3) h_c is the coefficient of convection heat transfer from the hot gas to the thermometer. A number of equations have been given by various investigators[2, 5, 23, 24] for the determination of h_c. One form given by C. S. Robinson is that of Equation (4):

$$h_c = \frac{0.44V^{0.8}T^{0.5}C_p(m - 0.081)}{M^{0.1}(m - 0.027)} \tag{4}$$

where h_c = Btu/ft²hr °F;
V = lb gas/ft²sec ("mass" flow or "mass" velocity);
T = temperature of gas, (°R);
C_p = specific heat of gas at constant pressure;
m = mean hydraulic radius of the gas passage (ft);
M = molecular weight of the gas.

A simpler formula, Equation (5), has been given by Haslam and Chappell[24]:

$$h_c = \sqrt{\frac{T_m V}{D}} \tag{5}$$

which was derived from Equation (6) by making several assumptions.

$$h_c = 0.51T_m\left(\frac{V^{0.67} - 0.09\log D}{D^{0.6}}\right) \tag{6}$$

where D = diameter of thermometer (inches);
T_m = °R (°F abs.) mean temperature of gas and thermometer.

Thus by determining h_c from Equation (4), (5), or (6) and using Equation (3), if all other factors are known, the unknown temperature, T_g, may be calculated.

The effective temperature of the wall, T_w, is in many cases very difficult to determine. Where the thermometer is in a small chamber whose walls are uniform in temperature, it is possible to obtain the wall temperature with a fair degree of accuracy. However, the determination of the effective wall temperature, of say a stoker-fired furnace having a fuel bed, refractory walls, and water-walls, together with variable and indeterminate layers of more or less impermeable gases, all at different temperatures, is almost impossible. Even if each of the different types of surfaces was at a uniform temperature it would be necessary to obtain their areas and respective solid angles with respect to the thermometer (or thermocouple). Thick layers of gases would also influence the values, since the thicker the gas layer the less the transmission of radiant heat.

Thus, if it were desired to correct by calculation the reading of a bare thermocouple located under boiler tubes in a furnace, using the foregoing equations, it would be necessary to know the following quantities: the radiating properties of the flue gas, the temperature, area, and respective solid angle of each kind of surface in the furnace, the area of the thermocouple, the thickness of the gas film around the thermocouple, the gas velocity, the emissivity of the thermocouple surface, the temperature of the gas, the temperature of the thermocouple, and the molecular properties of the gas.

It is manifestly impossible to determine, or even estimate all of these with any accuracy; hence, except in the most simple cases, this method of calculation must be discarded. Such calculations have been discussed by a number of investigators.[1,2,5,21,23,24,53B] An empirical method of correction will be developed and given later in Part 3.

8. The Radiation Pyrometer. The total radiation pyrometer[19,20] utilizes the Stefan-Boltzmann law, according to which the radiation of a substance is proportional to the fourth power of the absolute temperature. By suitable calibration, an instrument measuring the radiation can also be used to measure the temperature. Since gases are more or less permeable to radiation, although they radiate themselves, it is generally a solid surface temperature that is being measured. When a radiation pyrometer is pointed into a cavity through an opening, the results should be used with great care. If the radiation pyrometer is pointed at the opposite wall, momentary flames will frequently cause the readings to vary. In addition, the correct determination of the average gas temperature depends upon the thickness of the gas layer, the emissivity of the wall, and the temperature of the wall. Obviously, if the wall consists of water-cooled tubes the readings are practically worthless. If the wall is of air-cooled construction the temperature reading is likely to be low. If a solid refractory is in the region of a cold surface, the reading will be low because of the radiation of heat from the refractory to the cold surface. It is only where the refractory wall is well away from any cold surfaces and is in good thermal contact with the gases that any degree of reliance can be placed on the readings. Where it is desired to obtain the gas temperature in a steam-boiler furnace just before the gas enters the boiler tubes the method is evidently of questionable value.

9. The Optical Pyrometer. In the optical pyrometer[19,20] the temperature brightness of an incandescent filament is compared with the temperature brightness of the gas (necessarily luminous) sighted on. The same comments apply to this instrument that apply to the radiation pyrometer.

10. Color Pyrometer. For a long time temperatures have been estimated by the color, using the eye. This is, of course, inaccurate. Various types of color pyrometers have been developed. Recently a combined color and brightness (bioptical) pyrometer has been available.[53F,75-82,112] These are subject to the limitations discussed under the optical and radiation pyrometers. These instruments are generally calibrated for use when sighting on metals in a fluid state.

11. Spectral Line-reversal Method. A special case of this method known as the sodium line-reversal method has been frequently used,[38,42,43,44,50,53Q,91,93,101,109] and where applicable, it is of value. In this method a lamp filament is used, the temperature of which has been established by other methods. A spectroscope is sighted on the filament through a flame to which sodium has been added. As the temperature of the lamp filament is gradually increased, the bright sodium line, which shows on the continuous spectrum background, disappears when the temperature of the filament and flame are identical. If the filament temperature is increased, the sodium line will reverse. It has been found that this method gives results independent of the thickness of the flame, and it has been shown that it is not necessary to use sodium; other indicators may be used.

The method may be applied to luminous flames without the use of sodium.[63, 101] Variations of the method using photoelectric cell[63] photographic film, etc., have been frequently used[61, 62, 64-71] and are described by Ribaud, Laure and Gaudry.[53D]

12. **Heated Plate and Radiation Pyrometer.** In this method[7, 35] a wire or plate made of platinum is placed in the flame and heated by means of an electric current. If the platinum is colder than the flame, soot will form on it. If it is hotter soot will not form. The temperature of the plate may be measured by a radiation (or optical) pyrometer. This is essentially a laboratory method.

13. **Heated Wire and Vacuum Calibration.** This method as given by Griffiths and Awbery[41] and others,[53D, 59-62] is accurate, although somewhat of a laboratory method. A wire heated by an electric current is placed in a gas. Under steady conditions heat escapes from the wire in three ways: (1) radiation, (2) conduction to supports, and (3) convection to the gas. If the wire is at the temperature of the gas, the third cannot take place and all of the heat is radiated or conducted away. Identical conditions prevail in a vacuum. Thus if the point is found at which both the current and the temperature are the same for the wire in the gas as in a vacuum, this temperature is the gas temperature, because the equality of the temperature insures that the radiation and conduction terms shall be equal in the two cases, and the equality of current insures that the total heat dissipated is unaltered. Hence the convection is equal in both cases; and, since it is zero in the vacuum, it is also zero in the gas, so that the wire is at gas temperature. The temperature of the wire is determined by an optical pyrometer, although the apparatus can be arranged to use a thermocouple.[58]

14. **Interferometer.** Air temperatures based on the displacement of fringes in an interferometer[99, 100] have been measured close to solid surfaces.

15. **Photographic Method.** Neubert[97] has measured temperatures by photographing hot objects on plates sensitive to infrared radiation.

16. **Gas Temperature by Velocity of Sound.** According to Hartig and Wilcox[51, see also 52] the velocity of sound in a gas is proportional to the square root of the absolute temperature. This principle may be used to establish gas temperatures by measuring the velocity of sound. This method has attractive possibilities. It does not seem to have been previously tried, but is considered in a paper by C. A. Suits before the present Temperature Symposium.

17. **Gas Temperature by Thermal Conductivity.** Barnes and Bennett[74] have obtained the temperature of a flame from its thermal conductivity.

18. **Calorimetric Method.** A method of measuring the heat content of a given amount of gas, and from that calculating its initial temperature, has been developed by the Warmestelle der Julienhutte.[14, 53J, 72, 73] It appears to present difficulties too great to permit extended use.

19. **Flow of Gas through an Orifice.** H. Schmick[45] described a method in which the gas flows through a tube containing two orifices in series, the first orifice being at a location where the gas temperature was to be measured, and the second at a location of known gas temperature. He established the temperature at the

boiler fired by blast-furnace gas, using a high-velocity thermocouple as shown in Fig. 7 with a 16-mm diameter thermocouple element for gas temperatures.

According to the theory of the high-velocity thermocouple, the reading with no suction, *i.e.*, no gas flow past the thermocouple junction, will be considerably in error because of the poor convection heat transfer from the gases to the thermocouple. As the suction (or gas flow) is increased, the temperature indicated rises, until a value is reached where the convection heat transfer from the gases to the thermocouple is so great that the heat losses of the thermocouple by conduction and radiation are relatively negligible. A further increase in gas flow results in no appreciable temperature rise, thus showing that the true temperature has been reached. Fig. 8 shows a typical temperature curve given by Wenzl and Schulze.

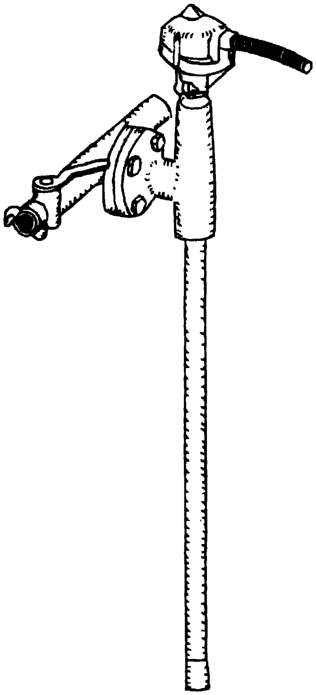

FIG. 5.

Commercial German high-velocity thermocouple for sale in the United States.

In using the high-velocity thermocouple this type of curve always results. It is the means of insuring a sufficiently high velocity. They found that it made no difference when the position of the hot junction of the thermocouple was varied from 1 inch to 11 inches from the open end.

Using a metal tube construction, their experiments showed that, due to the radiation of the tube, this form of a high-velocity thermocouple did not give the true temperature. They tried various types of shields (Figs. 9 and 10) finally concluding that the construction shown in the latter figure, using a number of small refractory tubes around the hot junction, was the best. The effect of this arrangement is simply that of a number of radiation shields. Their results were verified by Schack.[13, 53D] This type of construction may be termed a multiple-shield high-velocity thermocouple, conveniently designated as MHVT.

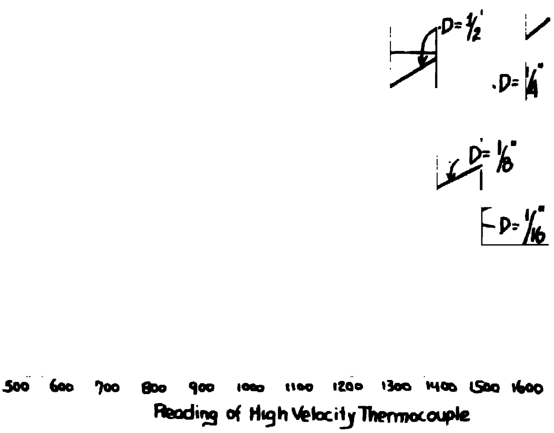

FIG. 6. Temperature difference between high-velocity thermocouple and adjacent bare thermocouples of various diameters (Haslam and Chappel).

For temperatures above the limits of a platinum platinum-rhodium thermocouple, an arrangement using a radiation pyrometer as shown in Fig. 11 was suggested. Various other investigators have suggested different forms. Fig. 12 shows a form without aspirator for use in pre-heated air ducts where the air is under pressure.[40] Nichols and Rice[22] have run tests in boiler flues using the type shown in Fig. 13 and have found errors of as much as 30 °F at 800 °F. Fig. 14 shows a form used by Freidrich[5] who has also given an extended mathematical treatment of his experimental investigations.

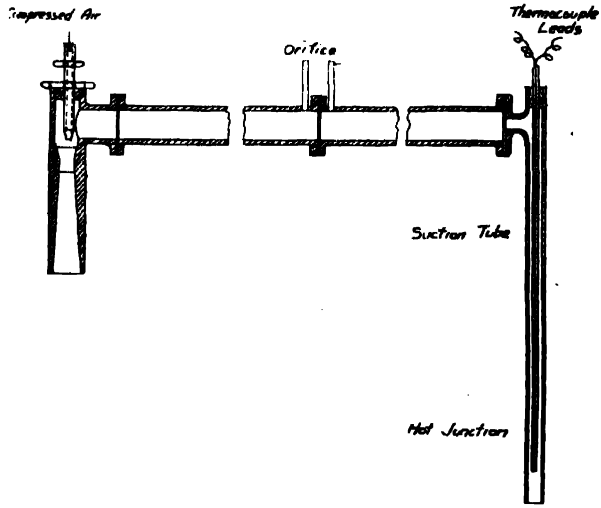

FIG. 7. Wenzl and Schulze high-velocity thermocouple.

G. V. Slottman[6] has described a number of tests. He found 100 °F error in a metal-lined stack. Fig. 15 shows results as given by him for measurements in the checkerwork of an open-hearth furnace.

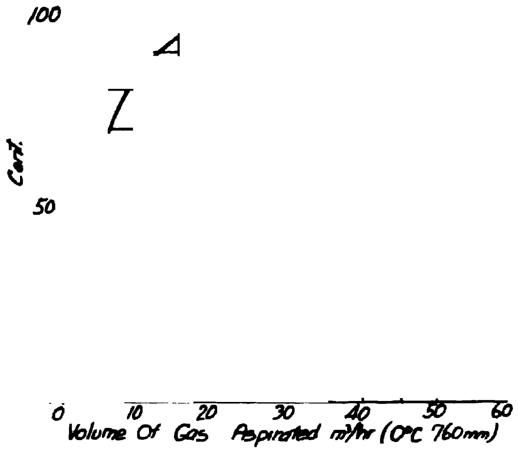

FIG. 8.

Relation between temperature indication and gas velocity for a high-velocity thermocouple (Wenzl and Schulze).

A number of high-velocity thermocouples of slightly different construction have been described and used by various investigators, such as Kuhn[113] in Germany, Lindmark[33] in Sweden, and others noted in the bibliography.

Where the readings of the high-velocity thermocouple have been inaccurate,[7,12,37,105] reference to the conditions of the testing would seem to show that the cause is probably (1) insufficient gas aspiration velocity, or (2) insufficient radiation shielding, *i.e.*, use of a single-shield HVT instead of the more accurate multiple-shield HVT (MHVT).

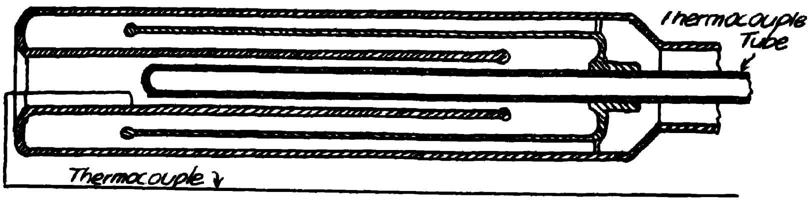

FIG. 9. Wenzl and Schulze triple-shield high-velocity thermocouple with auxiliary thermocouple for wall-temperature determination.

25. Heated-shield High Velocity Thermocouple. A further development of the high-velocity thermocouple has been suggested.[7,12,34,111] It consists simply of using the high-velocity idea in connection with a heated shield as shown in Fig. 16.* The shield is electrically heated for a length of about 12 inches by means of a Nichrome wire, the amount of heat being adjusted by means of a resistance. In one arrangement a thermocouple is attached to the shield and readings are taken while under suction when the central thermocouple and the shield thermocouple are at the same temperature.

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* Figures 16, 17, and 20 to 23 are reproduced by courtesy of the American Society of Mechanical Engineers.

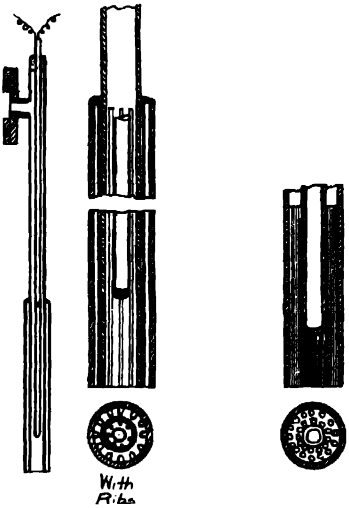


FIG. 10. Various multiple-shield high-velocity thermocouples (Wenzl and Schulze).

In a slightly different form a thermocouple is not used in the shield. This is based on the fact that when the radiation shield is at the same temperature as the thermocouple, no radiant heat exchange will take place no matter what the gas flow velocity may be. However, if one part is at a higher temperature than the other, a radiant heat exchange will occur, and the temperature indicated by the central thermocouple will vary with the velocity of the aspirated gas. If the shield is overheated it will be at a higher temperature than the central thermocouple, and will radiate heat to the thermocouple, thus causing its temperature to be somewhat

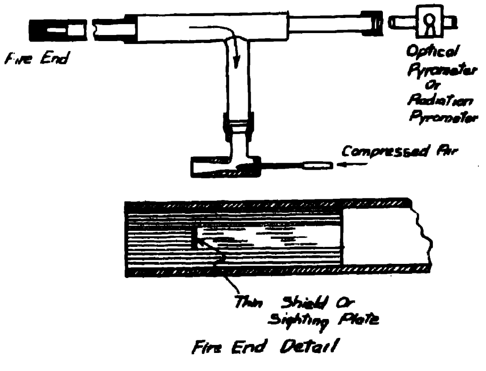

Fire End
Optical Pyrometer Or Radiation Pyrometer
Compressed Air
Thin Shield Or Sighting Plate
Fire End Detail

FIG. 11.

High-velocity pyrometer of Wenzl and Schulze for temperatures above the limits of thermocouples.

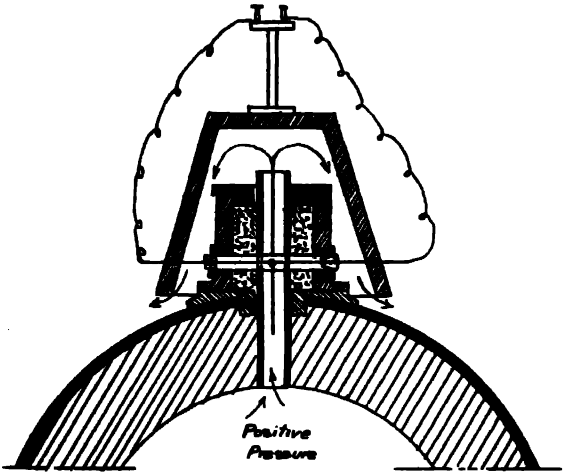


FIG. 12. High-velocity thermocouple as used in air ducts under pressure.

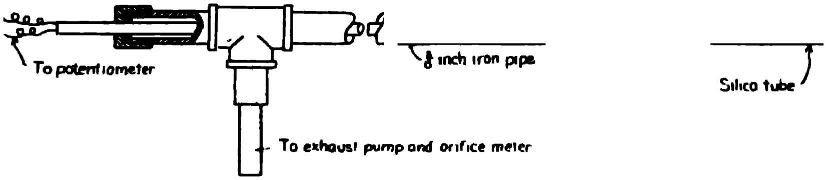


FIG. 13. Nichols and Rice high-velocity thermocouple for low temperature, as in steam-boiler flue-gas outlet ducts.

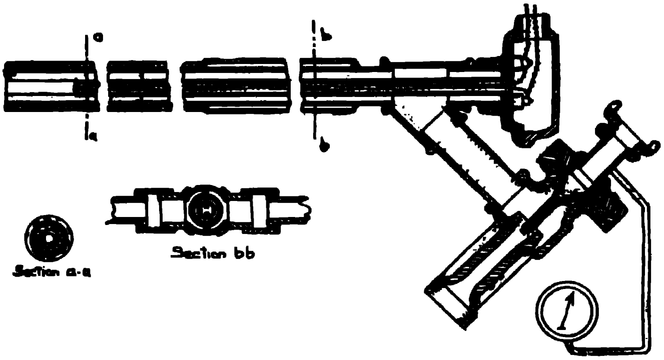


FIG. 14. Friedrich high-velocity thermocouple.

above the true gas temperature. If the velocity of the aspirated gas is now increased, the convection heat transfer between the gas and the thermocouple will be increased and the gas will cool the thermocouple, thus causing a lower temperature to be indicated. When the shield is at the same temperature as the thermocouple a variation of gas flow would not have this effect. On the other hand, when the shield was at a lower temperature than the central thermocouple, the reverse of that described above would occur. Thus, by varying the heating of the shield and the gas flow, the true temperature may be found. The method is too cumbersome, and is difficult where the gas temperatures are subject to rapid variation. Uchida and Tanabe [105] have used this method.

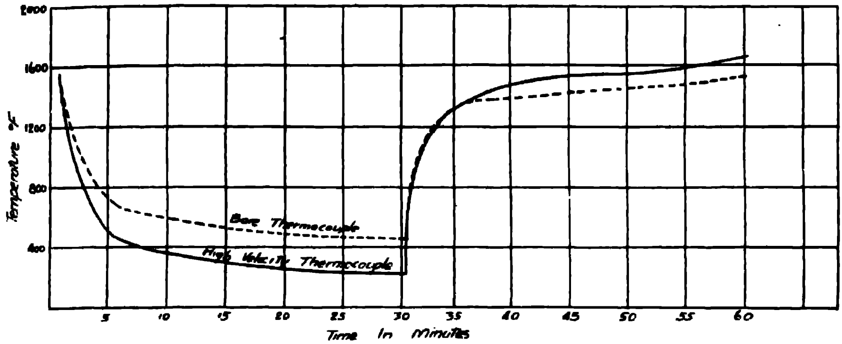


FIG. 15. Slottman temperature measurements in the checkerwork of an open-hearth furnace.

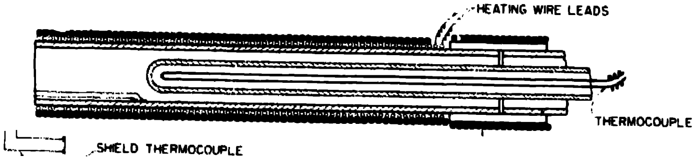


FIG. 16. Wenzl and Schulze heated-shield or compensated high-velocity thermocouple.

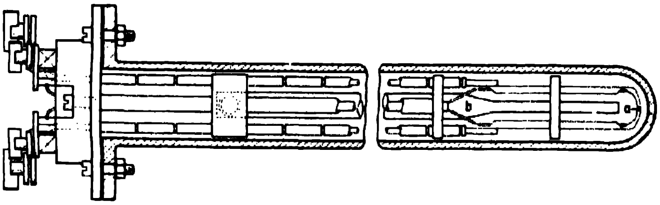


FIG. 17. Early commercial-type compensated high-velocity thermocouple (Schmidt).

Where the high-velocity thermocouple is to be used in a chamber where the walls are at a higher temperature than the gas, it is necessary to cool the thermocouple by a water jacket or the like, which is somewhat difficult.

Severinghaus has described[102] still another modification, consisting of co-axial Alundum tubes, the outer tube being heated. Thermocouples are located in the center tube and in the annular space between the tubes. Gas is aspirated through the tubes. Heating of the outer tube is varied until the thermocouples read the same. The two identical thermocouple readings may then be taken as establishing the gas temperature.

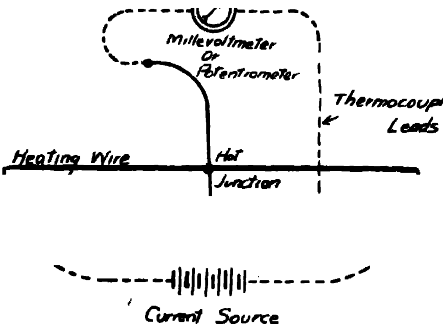


FIG. 18. Electrical circuit of thermocouple of Fig. 17.

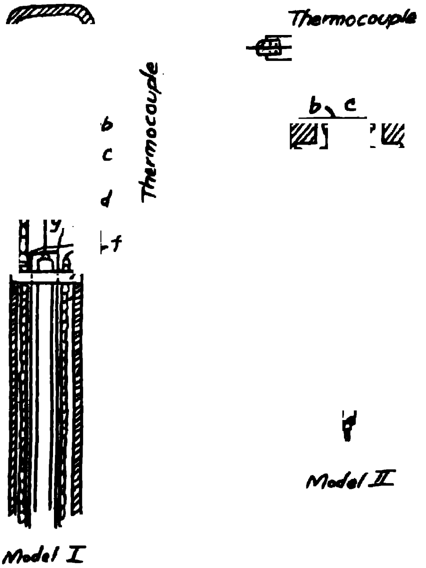


FIG. 19. Later Schmidt modifications of compensated high-velocity thermocouple.

26. Heated High-velocity Thermocouple. H. Schmidt[7,9,10,16,18,53L] has developed a very ingenious method which is a further development of the heating method. Fig. 17 shows one of the earlier forms. He has made use of an electrical circuit as shown in Fig. 18 by tapping the recording thermocouple directly across the heating wire. An improved form of the apparatus is shown in Fig. 19.

other methods are described in the original paper.[7] The principal objection to the method lies in that fact that it involves a variation of the gas flow with each reading. Schmidt has also described an automatic form of the apparatus.

II. Design and Construction of a Rugged High-velocity Thermocouple

Introduction

To evaluate the performance of a steam boiler it is necessary to measure the temperature of the gases at various locations in the furnace and in the gas passes of the boiler. This imposes rather severe conditions on any temperature-measuring device. The furnaces may be as much as thirty feet in width, and gas temperatures are frequently desired at location across this width in order to determine a complete "gas-temperature traverse." The majority of large modern units burn pulverized coal, so that the gases contain appreciable amounts of coal-ash or slag in suspension, which may be solid or plastic depending on the temperature. Temperatures range from about 3200 °F, occasionally encountered at a burner, down to room temperature. Test equipment used must be sufficiently rugged to stand up under everyday conditions of operation in a boiler-room.

None of the temperature-measuring devices previously described was suitable for this application. The various optical methods did not give temperature "traverses," and they were subject to errors due to the presence of relatively "cold" water-tube walls. Many of the methods are laboratory methods and not applicable to "flames" twenty or thirty feet across. Wall openings are generally limited, so that it is not possible to sight through a "flame" to apparatus on the other side of the flame. Above 1500 °F, some form of water-cooling is practically essential for any temperature-measuring device. Above 2400 °F, slag in the gases plugged most kinds of the previously suggested high-velocity thermocouples in a minute or two; and since these were not designed for ready repair, the reconstruction of the instrument required prohibitive lengths of time.

None of the foregoing having proved entirely satisfactory, a form of high-velocity thermocouple was developed during the last nine years. It has been in very frequent use over that time, and as thousands of readings have been taken, its characteristics are rather well known. It is the kind[106] first used in the American Society of Mechanical Engineers Furnace-Radiation-Committee investigation in 1935.[107]

This high-velocity thermocouple is of the single radiation-shield class, and can be used in slag-bearing gases up to the melting point of the platinum thermoelement (3190 °F). As noted in the preceding discussion of the high-velocity thermocouple, that with the single radiation-shield (HVT) is not as accurate as the one with the multiple-shield (MHVT). The MHVT is, however, not practical for extended use, as the shields would have to be replaced after every reading in slag-bearing gases. The HVT is more rugged, and replacement of the single radiation-shield is simpler. It is possible to determine the approximate error of the HVT, and since it seems to be the most accurate device next to the MHVT[108] the HVT has been adopted for routine testing.

Construction Details of High-velocity Thermocouple

The general arrangement is shown in Fig. 20, and the details of construction are such as to facilitate repair when the instrument becomes plugged or damaged by slag.

The gases are drawn through a water-cooled tube by means of an aspirator operated by compressed air. At the furnace end, a thermoelement hot junction surrounded by a porcelain radiation-shield is heated by the high-velocity gases flowing past.

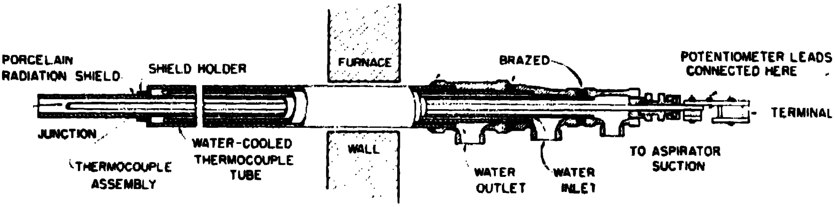


FIG. 20. Water-cooled high-velocity thermocouple developed and recommended for rugged general-service use.

The thermoelement runs from the hot junction through two-hole porcelain insulators to the terminal end of the water-cooled thermocouple tube. The length of the water-cooled thermocouple tube is as desired. Water-cooled tubes have been constructed as short as 3 ft and as long as 20 ft. With the longer lengths of tubing larger sizes must be used, to assure adequate water circulation.

It has been found that three sizes of water-cooled tube are adequate for practically all boiler test purposes. These are designated by the outside diameter of the tubing used, 1 inch, $1\frac{1}{4}$ inch, and $1\frac{3}{4}$ inch. The 1-inch size is used where a short, small-diameter tube is required; the $1\frac{1}{4}$-inch size for lengths not above 12 ft long or temperatures above 2600 °F. Above 12 ft long and 2600 °F, the $1\frac{3}{4}$-inch size is advisable, to provide adequate water-cooling. The sizes of the inner tubes for each of the three outer tube sizes are shown in Fig. 24. The tubing may be either brass or steel. The steel is stronger than the brass, but will rust. At the outer end of the water-cooled thermocouple tube the brass tubes fit into tee connections as shown in Fig. 20. The outlet ends of these tees are connected to the cooling-water lines.

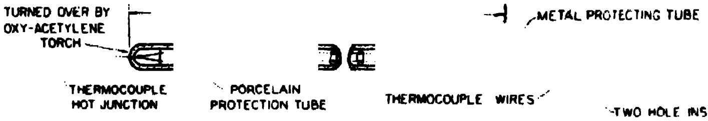

TURNED OVER BY OXY-ACETYLENE TORCH
METAL PROTECTING TUBE
THERMOCOUPLE HOT JUNCTION
PORCELAIN PROTECTION TUBE
THERMOCOUPLE WIRES
TWO HOLE INSULATOR

FIG. 21. Detail of hot-junction end of thermocouple of Fig. 20.

The sizes of the pipe "tee" fittings used in the 1-inch tube are as follows, the through-run opening being given first: $\frac{3}{4}$ by $\frac{1}{2}$ by $\frac{3}{4}$ in, with the first $\frac{3}{4}$-in opening drilled to $1\frac{1}{32}$ in and with the $\frac{1}{2}$-in opening drilled to $\frac{25}{32}$ in; $\frac{1}{2}$ by $\frac{3}{8}$ by $\frac{3}{4}$ in, with the $\frac{1}{2}$-in opening drilled to $\frac{25}{32}$ in; and $\frac{3}{8}$ by $\frac{3}{8}$ by $\frac{3}{8}$ in. A $\frac{3}{8}$ by $\frac{1}{8}$-in bushing is also required. The sizes of the pipe "tee" fittings used in the $1\frac{1}{4}$-in tube, the through-run opening being first, are: 1 by 1 by $\frac{3}{4}$ in, with the first 1-in opening drilled to $1\frac{9}{32}$ in; $\frac{3}{4}$ by $\frac{1}{2}$ by $\frac{3}{4}$ in, with the first $\frac{3}{4}$-in opening drilled to $1\frac{1}{32}$ in; and $\frac{1}{2}$ by $\frac{1}{2}$ in. A $\frac{1}{2}$ to $\frac{1}{8}$-inch bushing is also required. The sizes of the pipe "tee" fittings used in the $1\frac{3}{4}$-in tube, the through-run opening being first, are: $1\frac{1}{2}$ by 1 by $\frac{3}{4}$ in, with the $1\frac{1}{2}$-in opening drilled to $1\frac{25}{32}$, and the 1-in opening drilled to $1\frac{9}{32}$ in; 1 by $\frac{1}{2}$ by $\frac{3}{4}$ in, with the 1-in opening drilled to $1\frac{9}{32}$ in; and $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{3}{4}$ in. A $\frac{1}{2}$ to $\frac{1}{8}$-inch bushing is also required. The entire assembly is brazed to withstand

150 lb per sq in water pressure. The tubes are kept properly located by irregularly spaced "nibs" of braze metal. The ¼-in copper-tubing fittings used on the terminal end are drilled to take ¼-in tubing and have a ⅛-in pipe thread on one end. This fitting is of the brass compression-washer type.

The thermoelement runs from the hot junction through two-hole porcelain insulators to the terminal end. As shown in Fig. 21, the two-hole insulators at the hot end are surrounded by a protecting tube to keep the hot gases and slag from contaminating the thermoelement. The porcelain two-hole insulators are 3 mm outside diameter with 0.85-mm holes. Insulators of this size may be used throughout, from the hot end to the terminal at the cold end. It is difficult, however, to thread 22 B. & S. gage wire through an 0.85-mm hole. Because of this it may be necessary to use 3.0-mm O. D. by 0.85-mm I. D. insulators for a distance of 36 in at the fire end, and 3.75-mm O. D. by 1.00-mm I. D. by 12 in long porcelain two-hole insulators for the remainder of the length extending to the terminal end.

The porcelain protecting tube, which is 5 mm O. D. by 4 mm I. D. and 12 in long, readily fits over the 3-mm double-bore insulators. This protection tube is closed at the fire-end (the end having the thermocouple hot junction). Because of slag impingement, these protection tubes require frequent replacement at high temperatures. It is not necessary to use a high-quality porcelain, nor is it advisable because of the cost. It has been found that low-priced single-bore porcelain tubes are quite satisfactory. The ends are closed by use of an oxyacetylene flame or a porcelain plug. The plugs are held in place by refractory porcelain cement. The porcelain protection tube also serves as a small heat reservoir, thus tending to smooth out extremely rapid variations in indicated gas temperature which might result if the thermoelement were used bare.

From the end of the porcelain protecting tube to the terminal end, the two-hole insulators are covered with a ¼-in 18 B. & S. gage brass protecting tube to prevent moisture condensation on the thermoelement wires which, if permitted, would set up a battery action that would result in erratic readings.

The thermoelement consists of a 0.6-mm diameter platinum, platinum-10-per-cent-rhodium thermocouple 36 in long welded at one end to form the hot junction and silver-soldered at the other end to 22 B. & S. gage alloy extension-lead wire which runs to the terminal end. The extension-lead wires are in a relatively cool zone, as the gases cool very rapidly after entering the high-velocity-thermocouple tube.

Because of the long length of high-velocity-thermocouple assemblies, in making up thermoelements for use in these assemblies, it is advisable to use relatively short 36-in lengths of platinum, platinum-10-per-cent-rhodium wire, and attach this wire to extension-lead wire (frequently termed compensating-lead wire) of the same diameter, extending the lead wires to outside of the high-velocity-thermocouple assembly.

While it is easy to weld the hot junctions of platinum wire to platinum-10-per-cent-rhodium wire, it is very difficult to weld the low-melting point copper-alloy extension wire to either of these high-melting-point platinum wires. The attachment of the extension leads to the platinum (or platinum-10-per-cent-rhodium) wires may be readily done by the use of ordinary silver solder. A small oxyacetylene flame may be used, using the outside edges of the flame. The copper-alloy wire tips are first coated with silver solder. Then the platinum and copper-alloy wires are butt-jointed and thus silver-soldered together. The joint should be of little, if any, larger diameter than the wire. In case the joint thus made is a little over-size, the excess may be filed off with a common auto magneto or ignition file.

This type of joint has been tested from a thermoelectric standpoint, and it was found (as would be indicated by theory) that this joint of "foreign" material has no effect on the temperature indications of the thermoelement, if the joint does not exceed a temperature of 400 °F. In fact, common lead solder might also be used, but this is inadvisable, as the material is weak and the melting point is low.

The characteristics of extension-lead wire for platinum thermoelements are such that a thermoelement made of this wire will give exactly the same emf-temperature relation as a platinum, platinum-10-per-cent-rhodium thermoelement. However, the two leads should be used as a pair as the wires are not necessarily individually compensating.

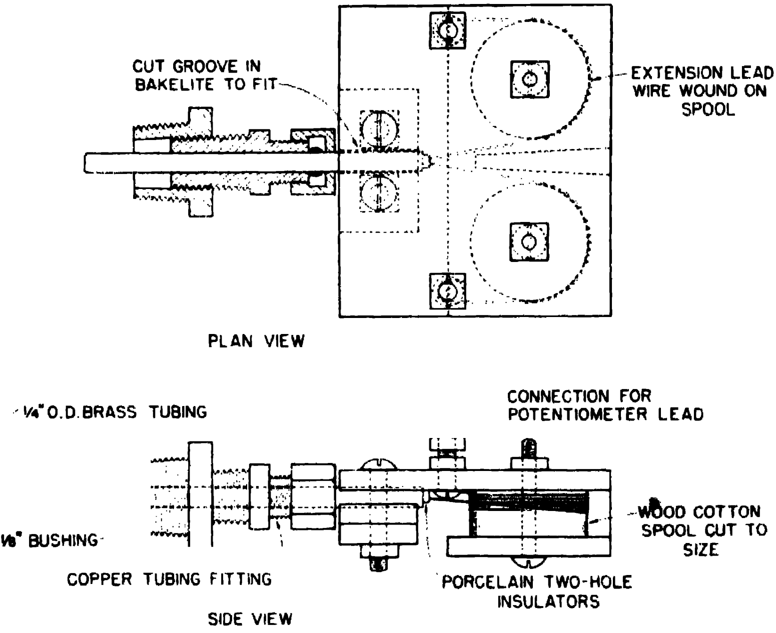

CUT GROOVE IN BAKELITE TO FIT
EXTENSION LEAD WIRE WOUND ON SPOOL
PLAN VIEW
1/4" O.D. BRASS TUBING
CONNECTION FOR POTENTIOMETER LEAD
1/2"-1/8" BUSHING
WOOD COTTON SPOOL CUT TO SIZE
COPPER TUBING FITTING
PORCELAIN TWO-HOLE INSULATORS
SIDE VIEW

FIG. 22. Detail of terminal of thermocouple of Fig. 20.

Platinum thermoelements should not be exposed to furnace gases. A short period of exposure is sufficient to enable the wires to absorb gases which change the standard temperature-millivolt calibration. This contamination usually causes the thermoelement to read low, by as much as 100 °F. When this occurs the remedies are: (1) cut off the contaminated portion; (2) electrically anneal at 2700 °F for 20 minutes and check for homogeneity, removing sections of wire only if the annealing has failed to restore the wire. The second is best done in the laboratory.

To determine whether a platinum thermocouple is maintaining the calibration: (1) comparison may be made against a "standard" or "check" thermoelement in a small electric calibration furnace; or (2) the homogeneity test may be applied. The first is the method most readily used in the field and it should be done frequently. The homogeneity test is at present restricted to the laboratory. If a thermoelement passes the homogeneity test satisfactorily, it will also be accurate on direct calibration.

Quoting the homogeneity test as described by the U. S. Bureau of Standards,

> "a short length of each thermocouple wire is selected as a standard reference specimen. These lengths may be cut from the uncontaminated cold-junction ends of the couple, and one set may be used repeatedly for various couples of the same type. One end of the standard wire—for example, the pure platinum wire—is placed in contact with a section of the corresponding wire of the thermocouple, and the emf is observed between the cold-junction end of the thermocouple wire and the free end of the standard wire when the point of contact between the standard and the thermocouple is heated to some convenient high temperature, maintained constant. The point of contact of the two wires is then moved to a different section of the thermocouple wire and the process continued until the platinum wire of the thermocouple is completely explored. The process is repeated for the alloy (Pt−10 per cent Rh.) wire of the couple, except that in this case the specimen of the alloy wire is used as the standard."

The homogeneity test is undesirable for field checking purposes as it requires removal of insulators. For use below 2000 °F a 22 B. & S. gage, Chromel-Alumel thermoelement may be substituted for the platinum thermoelement.

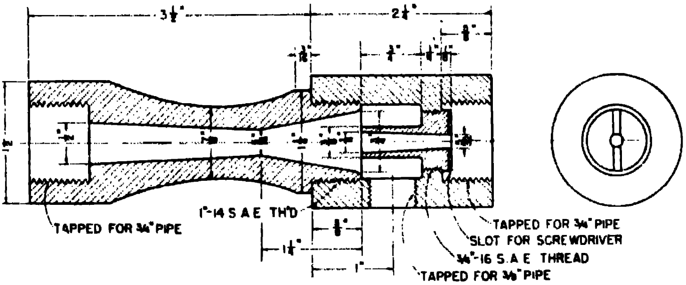


Fig. 23. Detail of aspirator of thermocouple of Fig. 20.

The end of the porcelain protecting tube is kept ½ inch from the open end of the porcelain radiation-shield. The porcelain radiation-shield is ¾ in O. D. by ½ in I. D. by 4 in long. It is cemented with porcelain cement into the radiation-shield holder which is of ¾-in alloy pipe ¾ in long.

The construction of the terminal for the lead wires is shown in Fig. 22. The end of the 22-gage extension-lead wire from the thermoelement is wound on a spool and then connected to a terminal to which in turn is connected a potentiometer to measure the millivoltage set up by the thermoelement junction.

The construction of a suitable compressed-air aspirator for operation of the high velocity thermocouple is shown in Fig. 23.

Operating Precautions. The construction described above has been adopted to facilitate the obtaining of temperature readings under severe slagging conditions in the furnaces of steam boilers. In operation under adverse slagging conditions the porcelain radiation-shield and the porcelain protecting tube, after one or two readings, become fouled with fluid or sintered slag which obstructs the gas flow. It is then necessary either to scrape the slag from these porcelains or, where this cannot be done, to replace the porcelain. Thus, for extended testing, an ample supply of porcelain radiation-shield and porcelain protecting tubes is required.

The platinum thermoelement wire must at all times be protected from the action of slag and gases by the protection tube, which cannot be used if cracked, because the metal becomes contaminated and inaccurate readings result. If the wire has been exposed for a period of time, it should be checked or calibrated, or the contaminated portion should be cut off and a new hot junction made.

The thermoelements are subject to breakage at the hot junction. A few feet of extra extension-lead wire are coiled around the spool provided at the terminal end, and, whenever the thermocouple wire is broken, it is a relatively simple matter to uncoil the amount needed, move the insulators back and make a new weld at the hot junction.

Sufficient water should flow through the tubing so that it is possible to place the hand on the outlet pipe, the water lines being such that the outlet tube is connected to the drain.

In operation, as the gas velocity is gradually increased, the temperature indication given by the thermoelement will also increase. The amount of increase gradually becomes less until, at some value of gas velocity, further increase does not result in an increased temperature indication. The aspirator of Fig. 23 is so designed as to give considerably more than this minimum velocity when opened wide. It takes about one minute for the thermocouple to reach full reading after the suction has been turned on full. The suction should be "on," only during the time that the readings are being taken, to avoid plugging the radiation shield with ash particles. When particles do lodge in the shield, they can sometimes be removed by putting a plug in the aspirator exhaust, thus blowing compressed air back through the high-velocity-thermocouple tube. This should be done with caution to avoid blowing the insulators out the end. Ordinarily, sintered ash may be removed by means of a bent wire.

In gas- and oil-fired furnaces the high-velocity-thermocouple assembly may be left in operation indefinitely, but in the furnace of coal-burning units it is generally necessary to limit the use of the high-velocity thermocouple to the time of a reading, it then being removed and cleaned if necessary. Under conditions where the ash is fluid it will be possible to take only a few readings. Then the old refractory radiation-shield and end-protecting tube, if covered with slag, must be removed and new refractory tubes inserted.

In practice the suction is checked before and after every reading by putting the palm of the hand over the radiation shield. If a vacuum is not felt, the apparatus is examined for obstruction. Readings obtained with amounts of slag in the end sufficient to decrease the gas velocity appreciably cannot be accepted as accurate and must be repeated. Thus, under adverse conditions as regards slagging, a number of trials may be required to obtain a single reading. The aspirator is ordinarily not mounted on the end of the high-velocity thermocouple, as its weight would cause difficulty in handling. Instead, a short length of hose connects the end of the high-velocity thermocouple to the aspirator.

For operation at temperatures 2700 °F or over, some difficulty may be encountered due to the breakage of the porcelain radiation-shield caused by thermal shock on insertion in a furnace. This may be overcome by pre-heating the radiation shield by electricity or gas, or more easily by coating the radiation-shield with wet porcelain cement. The time required to dry this cement on insertion in a furnace permits the porcelain radiation-shield to heat without cracking.

Comparison with an "ordinary" thermocouple is readily made by tying the ordinary thermocouple to the outside of the high-velocity-thermocouple tube, allowing the hot junction to project six inches beyond the radiation-shield. The tube keeps the leads cool. Readings taken simultaneously on the ordinary and on the high-velocity thermocouple will indicate, at readings of say 2000 °F of the ordinary thermocouple, high-velocity-thermocouple readings of the order of 2225 °F in furnaces, and 2325 °F in the cavities of boiler-tube banks. This difference in temperature depends, of course, on the surroundings of the thermocouples and will vary with the location.

In order to insert the high-velocity thermocouple in a furnace through a door, a removable asbestos or Transite panel, with a small hole for insertion of the thermocouple, is constructed and used to replace temporarily the door during readings. This eliminates difficulty due to inward air leakage. For permanent installations a two-inch nipple with a removable cap on the outside may be built into the wall.

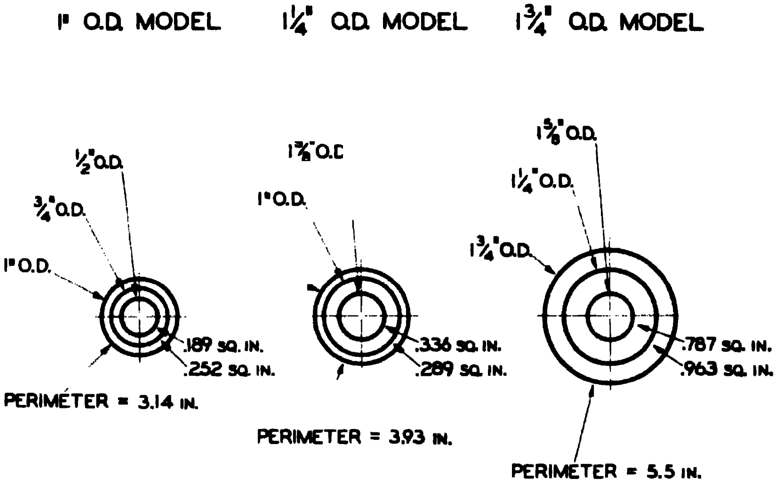


FIG. 24. Various sizes of water-cooled tubes for thermocouples of Fig. 20. Outside exposed tubes 18 B.&S. gage. All other tubes 22 B.&S. gage.

By a suitable arrangement of fittings at the outlet end, the high-velocity-thermocouple tube may be used for gas analyses, it being necessary to reduce the aspiration to a suitable value in order to do so.

Potentiometers, because of their rugged construction and continued accuracy, are preferred as indicating instruments.

At low temperatures non-water-cooled constructions may be employed, but ordinarily these are not very satisfactory on account of the necessity of handling hot tubing.

The method described is certainly not simple compared to that often employed of simply fastening ordinary bare thermocouples in the gas passage of the duct where the gas temperature is to be measured; but where accuracy is required it seems to be worth the difficulty involved.

Numerous tests by the author indicate that the error ordinarily experienced in measuring the steam-boiler outlet gas temperatures at say 600 °F by the usual means is only about 10 °F low. This agrees with the findings of Nichols and Rice.[22] On this basis it would seem unnecessary to use the apparatus described for ordinary steam-boiler efficiency tests. On the other hand, in heat-transfer tests the gas temperature entering the first row of boiler tubes is frequently desired and is obtained without great error by this method. In numerous other industries such as oil refining, steel production, glass melting[16,17] and the like, the method is of increasing importance.

The high-velocity thermocouple is a test device and is not suitable for permanent installation, as it requires considerable attention.

III. Development of Empirical Correction

High-velocity-thermocouple Correction

As discussed in Part I, undoubtedly the best temperature-measuring instrument is the type of high-velocity thermocouple shown in Fig. 10; but it has such small gas passages as to be impractical for use in furnace gases containing slag or ash particles. For this reason the simple, rugged single-shield type of high-velocity thermocouple shown in Fig. 20 has been used.

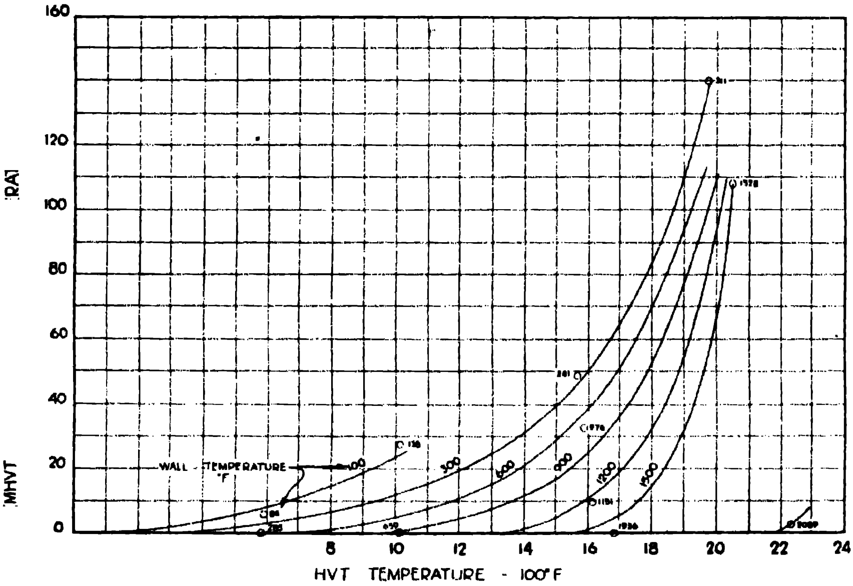
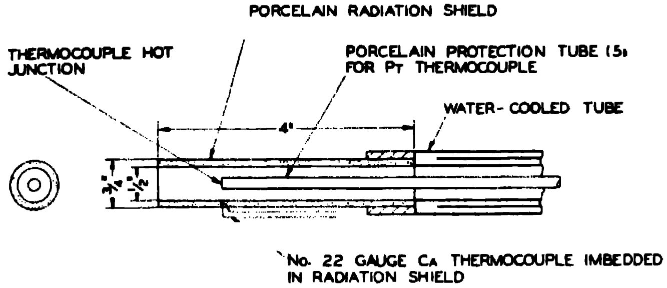


Fig. 25. Difference between readings of high-velocity thermocouple (HVT) and multiple-shield high-velocity thermocouple (MHVT) temperatures as a function of HVT shield temperature (Numbers beside data points correspond to HVT temperatures).

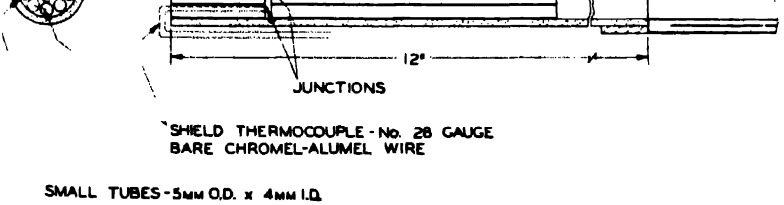
It has been demonstrated[108] that this single-shield high velocity thermocouple (denoted as HVT) reads somewhat less than the true gas temperature, and that the latter is probably approached very closely by the multiple-shield high-velocity thermocouple (denoted as MHVT) of the type shown in Figs. 10 or 26.

It is possible to establish a relation between the MHVT and the HVT readings As shown in Fig. 25, the error is appreciable for 4-inch-square ducts having very cold walls. This particular case is seldom met.

In engineering practice, to enable calculation of heat-transfer rates, it is desirable to measure gas temperatures in steam-boiler furnaces and boiler gas passes Since these furnaces and passes are very large, the curves of Fig. 25 are not appli cable. The walls, while frequently comprising water-cooled tubes, may be covered with various amounts of slag which increases their effective surface temperature, thus decreasing thermocouple error.


PORCELAIN RADIATION SHIELD
THERMOCOUPLE HOT JUNCTION
PORCELAIN PROTECTION TUBE (5) FOR Pt THERMOCOUPLE
WATER-COOLED TUBE
4"
No. 22 GAUGE CA THERMOCOUPLE IMBEDDED IN RADIATION SHIELD

FIRE-END OF HIGH VELOCITY THERMOCOUPLE-(HVT)


MIDDLE OR GAS THERMOCOUPLE - No. 28 GAUGE BARE CHROMEL-ALUMEL WIRE
WATER-COOLED TUBE
1½"
4½"
12"
JUNCTIONS
SHIELD THERMOCOUPLE - No. 28 GAUGE BARE CHROMEL-ALUMEL WIRE
SMALL TUBES - 5MM O.D. x 4MM I.D.

FIRE-END OF MULTIPLE-SHIELD HIGH VELOCITY THERMOCOUPLE-(MHVT)

FIG. 26. Detail of hot junctions of high-velocity thermocouple and of multiple-shield high-velocity thermocouple.

To obtain a measure of HVT error in service, simultaneous readings were taken by HVT and by MHVT in a number of boiler furnaces. The MHVT readings were obtained with extreme difficulty; frequently only two or three readings were taken before it was necessary to renew completely the fire-end radiation-shields and thermocouples. The actual construction of the HVT and MHVT used is described in another paper "Accuracy Tests of the High Velocity Thermocouple."[108] Fig. 26 is a reproduction of Fig. 5 from that paper, showing construction of the fire-ends of the HVT and MHVT.

It was possible to draw an average curve through the data, thus giving a correction to add to HVT readings to obtain equivalent MHVT readings. The MHVT readings may be assumed to be very close to true gas temperature. This curve marked MHVT is shown on Fig. 27 in addition to other correction curves to be described below. For steam-boiler furnaces and large cavities in boiler convection tube-banks this curve may be used. The HVT correction (amount to add to HVT temperature to obtain MHVT temperature) varies with HVT temperature, but appears to be not more than 100 °F at any temperature.

Correction of Readings of Other Pyrometers to HVT Base. Frequently test data are obtained by other types of temperature-measuring devices than the high-velocity thermocouple.

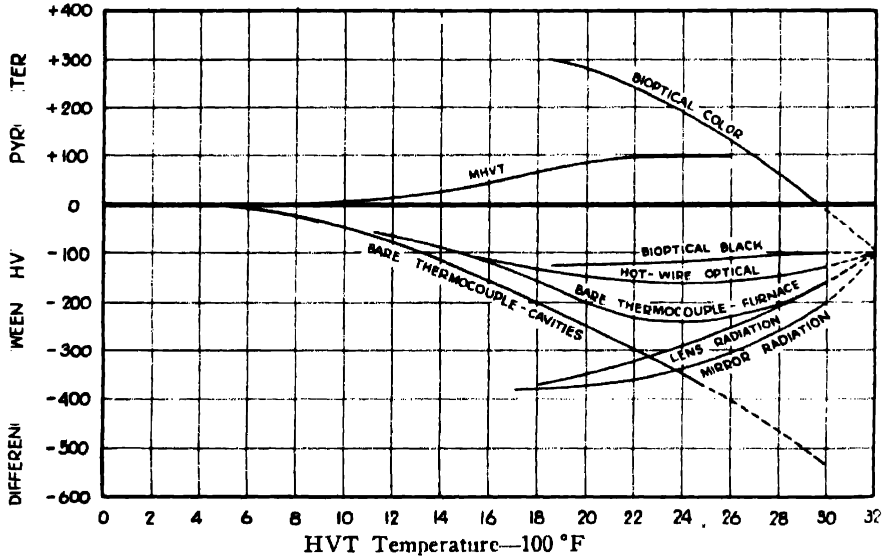


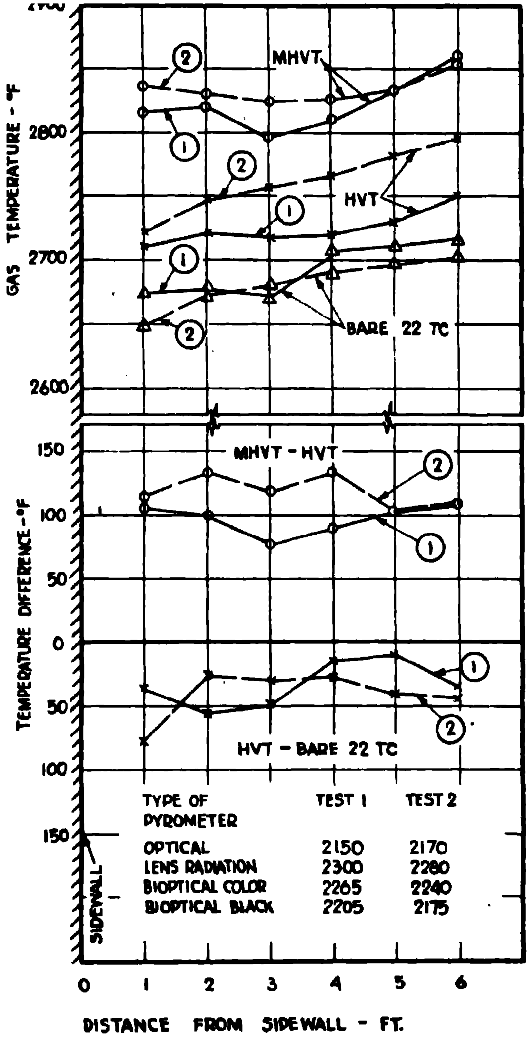
Fig. 27. Comparison of temperature indications of various types of pyrometers in gases of steam-boilers.

As high-velocity thermocouples involve considerable effort in use, temperatures are sometimes read by bare thermocouple or by optical pyrometers. For this reason it is desirable to know the approximate relation between the temperatures indicated by various kinds of pyrometers. The relation between the temperatures indicated by various types of temperature pyrometers is plotted in Fig. 27. These curves represent averages of hundreds of readings taken for more than fifteen steam-boiler tests, plus data from other sources.

The boilers on which test data were obtained were mostly pulverized-coal-fired units of widely different designs, but many data from oil-fired, stoker-fired and gas-fired units were also included. No consistent relation between mode of firing and pyrometer temperature relation was noted.

As previously mentioned, since the single-shield high-velocity thermocouple

(HVT) appears to give the most accurate readings next to the multiple-shield high-velocity thermocouple (MHVT), which cannot be satisfactorily used for routine work in slag-bearing gases, all corrections have been related to the HVT as a base. The correction values given by Fig. 27 are the values in degrees Fahrenheit



TYPE OF PYROMETER	TEST 1	TEST 2
OPTICAL	2150	2170
LENS RADIATION	2300	2280
BIOPTICAL COLOR	2265	2240
BIOPTICAL BLACK	2205	2175

Fig. 28.

Two series of typical MHVT, HVT and bare 22-gage thermocouple test data obtained in natural-gas-fired boiler furnace. Simultaneous optical and radiation pyrometer data are also shown for comparison.

to add or subtract from the HVT temperature to obtain the equivalent temperature reading of any other type of pyrometer.

Several kinds of pyrometers are represented in Fig. 27, including the combined color-brightness optical pyrometer ("Bioptical") which gives two readings, one known as color temperature and one known as blackbody temperature. Two different classes of radiation pyrometers are included, one of the "lens" type, in which a lens is used to focus the heat rays on the sensitive element, and the other the "mirror" type, in which a metal mirror is used to reflect and focus the heat rays on the sensitive element. The ordinary filament (hot-wire) optical pyrometer and bare thermocouples are also represented, the results being applicable for 14-gage (0.064-in) wire size and larger (due to accumulation of slag, etc., on wire).

In Fig. 27 a distinction is made between a "furnace," either primary or secondary, and a cavity in a tube bank such as occurs between tube banks. Small radiant passes such as are found in "open-pass" types of boilers may be classified as "cavities." Different curves are given for bare thermocouple temperatures, depending whether the measurement is made in a boiler furnace or in a cavity. The "cavity" bare-thermocouple plot is also applicable with less accuracy to measurements made between tubes (intertube).

The optical, radiation, and other pyrometer curves are applicable to both furnaces and "cavities," but ordinarily not to gases between closely-spaced tubes. The bioptical color temperature apparently reads appreciably above the MHVT or true gas temperature. This is presumably because this instrument is calibrated for the purpose of reading the temperatures of molten metals rather than of layers of gas or flame.

The dotted lines in Fig. 27 represent extrapolated and estimated values, there being little data above 3000 °F. Based on the apparent slope of the curves it would appear that in steam-boiler furnaces most of the temperature measuring devices will read about the same at 3200 °F.

These plots give an average correction between readings obtained by the given pyrometers. Individual determinations will vary from the corrections given, by plus or minus as much as 200 °F, but the average correction of a large number of readings may be expected to lie fairly close to the values given.

The plots give relations to be expected under average conditions. Where readings are taken under unfavorable conditions, adjustment should be made. Thus an optical pyrometer used to obtain the gas temperature of a clear gas in a very small cavity surrounded by clean, cold surface may be expected to read low. Similarly, the optical pyrometer will read high if sighted on the center of the flames issuing from a burner when viewed from an opening near the furnace exit, and a bare thermocouple in a well-cooled ash-pit through which little or no gas is passing will read high. These are abnormal conditions. Readings obtained under normal conditions are represented by the plots.

Although necessarily inaccurate it seems advisable to use these empirical corrections rather than to use the as-read values without any correction whatever. Actually no curves can ever be given to fit other than one very special case. Curves given for general conditions such as the above must be more or less inaccurate.

* * * * *

Discussion of this paper and the succeeding one are combined and follow the latter.

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Accuracy Tests of the High-Velocity Thermocouple

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Summary

It was desired to obtain a measure of the absolute accuracy of the high-velocity thermocouple (sometimes known as an aspiration pyrometer). Apparatus constructed and set up in the laboratory was so arranged that the true gas temperature in a 4-inch-square test section could be obtained by means of specially constructed temperature-measuring sections before and after this test section. Readings of a single-shield high-velocity thermocouple, a multiple-shield high-velocity thermocouple, and various sizes of ordinary bare thermocouples were compared. Results are valuable in estimating the errors involved in gas-temperature measurement by the use of these various types of thermocouples. Typical readings applicable to a 4-inch-square duct with walls at 311 °F are indicated by Fig. 7. The temperature differences thus shown will be much less in larger ducts having walls at higher temperatures.

Introduction

An ordinary thermocouple junction inserted in a furnace or duct carrying high-temperature gas can "see" the relatively colder walls. The thermocouple junction, although but a few hundredths of an inch in diameter, will radiate heat to this colder surface and thus will be cooled below the true temperature of the surrounding gas. The resulting error may amount to several hundred degrees.

This error may be decreased by the use of a "high-velocity thermocouple" that has a radiation insulating shield around the tip so that it will be able to "see" only a small portion of the cold walls. A stream of hot gases is then aspirated past the junction of the thermocouple at a high velocity. This further increases the heat transfer from the gas to the thermocouple tip, thereby causing the reading to approach more closely the true gas temperature.

The high-velocity thermocouple has been described more completely in another paper,[1] presented before this Symposium by one of the present authors, consequently the theory and actual construction of this device are not given here.

While several investigators in the literature, notably Wenzl and Schultze,[2] and Uchida and Tanabe [3] have published test data to indicate the inaccuracy of the high-velocity thermocouples used under certain conditions, their data were not as extensive nor as detailed as might be desired.

In order to permit a systematic variation in test conditions, equipment was designed and set up in the Barberton, Ohio, laboratory of The Babcock & Wilcox Co. The apparatus was constructed so as to permit considerable flexibility in testing with the exception that all measurements were made in a four-inch-square duct, a size appreciably smaller than that encountered in most engineering practice.

Apparatus

Fig. 1 shows a sketch of the apparatus used. The arrangement consisted essentially of a laboratory-type gas-fired furnace supplying hot gas serially to (1) an

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* Mr. T. P. Monahan of The Babcock & Wilcox Co. assisted in the laboratory work.

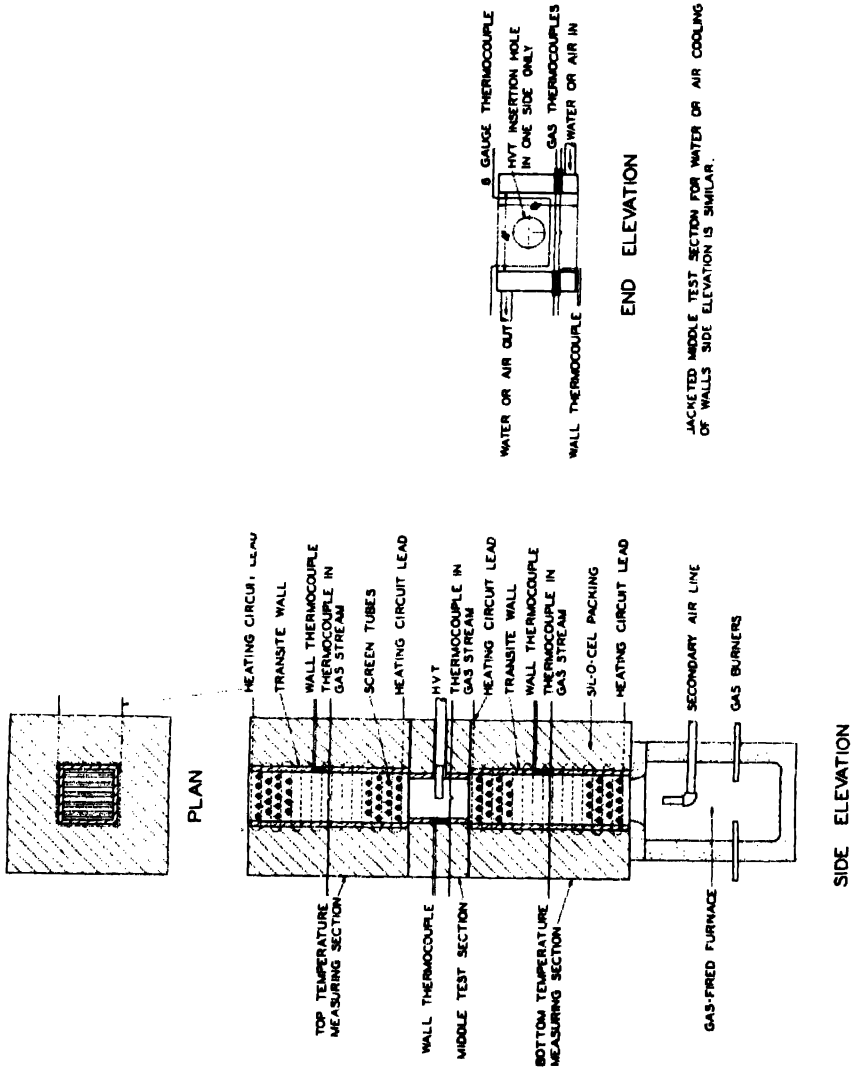


Fig. 1. High-velocity thermocouple laboratory test apparatus (4-inch-square test duct used).

initial bottom temperature-measuring section, (2) a middle test section, and (3) a top temperature-measuring section. The gas passage in all the middle sections was 4 inches square.

A measure of the true gas temperature was obtained by using the mean of the gas temperatures in the bottom and top temperature-measuring sections. Both the bottom and top temperature-measuring sections were made uniform-temperature enclosures to enable accurate temperature measurements to be made.

The gas temperatures in the bottom and top temperature-measuring sections of the test apparatus were measured by bare 22-gage Chromel-Alumel thermocouples, four in each section. These thermocouples were suspended in the duct as shown in Fig. 1, lead wires for each thermocouple passing through opposite walls of the duct. Thus no insulators were required on the thermocouple wires in the duct.

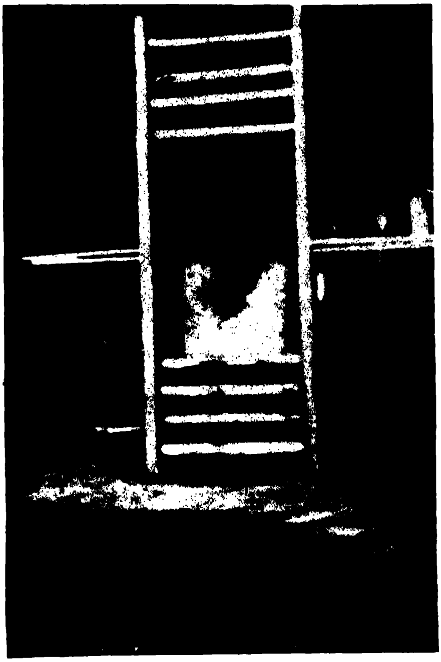


FIG. 2.

Upper (or lower) test section with side-wall removed.

Wall temperatures were taken by means of Chromel-Alumel thermocouples embedded in the Transite walls of the duct and coated with Alundum cement. Eight thermocouples of this type were placed in the walls of both bottom and top sections.

In order to maintain the walls at the same temperature as that of the gas, the walls were heated by means of a resistance coil to the temperature indicated by the gas thermocouples in the duct. "Screens" of Alundum tubes shielded the gas thermocouples from the hotter and colder portions of the duct above or below the section in which the temperature was being measured. Radiation effects being thus eliminated, these bare gas thermocouples were assumed to read the true gas temperature entering and leaving the middle or test section.

Fig. 2 is a photograph of a temperature-measuring section (either bottom or top) with the side removed to show the "radiation screen" tubes.

To keep the gas temperature drop between bottom and top sections to a reasonable value (less than 100 °F) it was necessary to limit the height of the middle test section to 6 inches or less. To attain a high mass-flow through the apparatus (thus decreasing the temperature drop across the test section) secondary air was supplied at the top of the gas-fired furnace.

The thermocouples under test were compared in the middle test section which was constructed with removable wall sections so that the temperature of the wall could be varied. Middle test sections of different types such as of Transite wall construction or of metal water-cooled or air-cooled construction were used. The temperatures of the middle test section walls in the case of the Transite walls were obtained by embedded Chromel-Alumel thermocouples coated with Alundum cement. In the case of the water-cooled or air-cooled test section the wall thermocouples were peened directly into the metal walls.

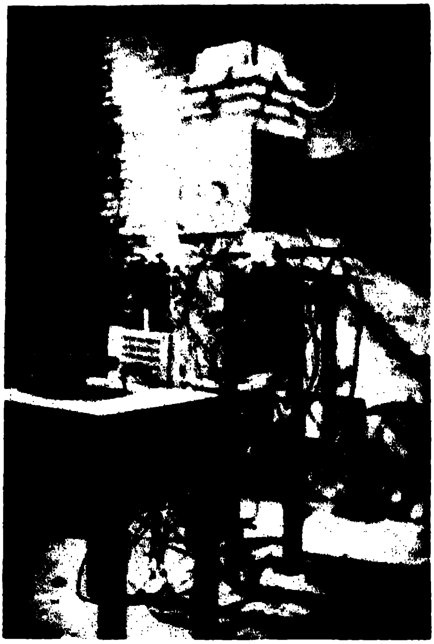


Fig. 3.

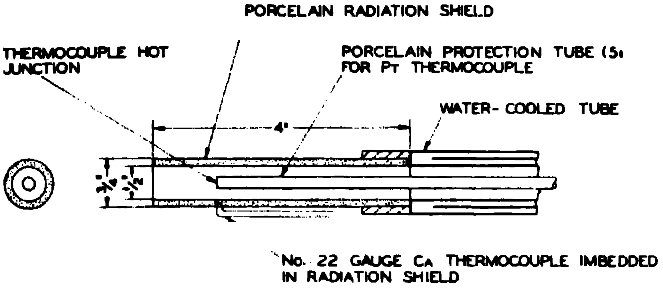
Photograph of laboratory test apparatus.

For comparative purposes four ordinary bare Chromel-Alumel thermocouples of 8, 14, 22 and 28 B. & S. gage respectively were suspended in the gas stream in the middle test section. These thermocouples were grouped as closely as possible just below an opening provided for insertion of the high-velocity thermocouple to be tested.

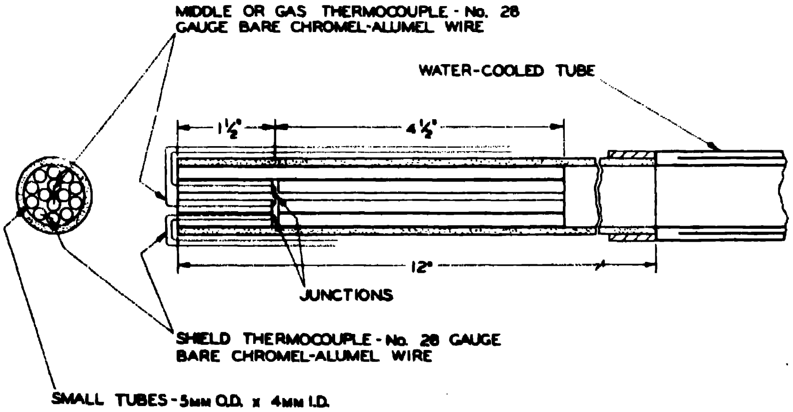
Fig. 3 is a photograph showing the assembled apparatus.

A water-cooled high-velocity thermocouple assembly, designated HVT, was used for the test work. This HVT was of the type used in field tests on steam-boiler furnaces. For field use a platinum, platinum-rhodium thermocouple, necessarily protected from gas contamination by a protection tube, has been used in the HVT so that readings may be obtained in gases having temperatures ranging from

3150 °F downward without the necessity of changing thermocouple wires. For the present tests in which the gas temperature was not raised above 2200 °F Chromel-Alumel thermocouple wire might have been used in the HVT instead of


PORCELAIN RADIATION SHIELD
THERMOCOUPLE HOT JUNCTION
PORCELAIN PROTECTION TUBE (5ı FOR PT THERMOCOUPLE
WATER- COOLED TUBE
4"
3/4"
1/2"
No. 22 GAUGE CA THERMOCOUPLE IMBEDDED IN RADIATION SHIELD

FIRE-END OF HIGH VELOCITY THERMOCOUPLE-(HVT)


MIDDLE OR GAS THERMOCOUPLE - No. 28 GAUGE BARE CHROMEL-ALUMEL WIRE
WATER-COOLED TUBE
1½"
4½"
12"
JUNCTIONS
SHIELD THERMOCOUPLE - No. 28 GAUGE BARE CHROMEL-ALUMEL WIRE
SMALL TUBES - 5MM O.D. x 4MM I.D.

FIRE-END OF MULTIPLE-SHIELD HIGH VELOCITY THERMOCOUPLE-(MHVT)

Fig. 4. Detail of hot junctions of high-velocity thermocouple and of multiple-shield high-velocity thermocouple.

the platinum thermocouple wires, but it was considered better to use exactly the same construction of HVT as that used in the field.

On all tests, unless otherwise noted, a 5-mm (0.197-in) O. D. porcelain protection tube was used in the HVT as a gas-contamination protection sheath for

Table 1. Summary of Data of Laboratory Test Series 1 to 4 Using Middle Test Section.

(Results as given in lines 21 to 25 are plotted in Fig. 5)

1	Test Series	1								
2	Kind of Test	Test Section Walls Water-Cooled								
	Data of Representative Runs									
3	Date	5-31-39		5-26-39		5-18-39		5-17-39		6-1-3
4	Time	11:20 AM	2:05 PM	10:40 AM	11:30 AM	2:15 PM	12:40 PM	2:35 PM	3:55 PM	11:15 AM
5	Gas temp entering test section	2203	2197	1648	1652	1044	1036	604	628	2236
6	Gas temp leaving test section	2020	2012	1584	1577	985	967	564	579	2070
7	Temp No. 8 ga TC in test section	1835	1835	1487	1497	960	950	563	581	1952
8	Temp No. 14 ga TC in test section	1895	1897	1522	1520	972	966	570	586	1990
9	Temp No. 22 ga TC in test section	1940	1920	1533	1538	993	990	586	607	2031
10	Temp No. 28 ga TC in test section	1990	1980	1558	1567	1004	1000	589	609	
11	HVT temperature	1959		1566		1002		588		2047
12	MHVT temperature		2094		1611		1013		610	
13	Mean of end temps = [(5) + (6)]/2	2111	2104	1616	1614	1014	1001	584	604	2156
14	(Mean of end temps) − (HVT or MHVT) = (13) − (11) or (12)	152	10	50	3	12	−12	−4	−6	109
15	Test section wall temp	311	310	242	247	138	135	84	88	1528
16	(MHVT) − (Test section wall temp) = (12) − (15)		1784		1364		878		522	
17	Radiation shield temp	1808	2080	1450	1595	929	1000	518	604	1940
18	Optical pyrometer temp test section	1607								
19	Velocity through HVT rad. shield ft/sec	507	130	282	93	242	55.5	151.3	32.3	110.8
20	Mass flow through HVT rad. shield lb/ft²hr	14450	5840	13080	5900	16300	4980	15500	4205	15410
	Average for all runs on each test series of which above are typical runs									
21	HVT temp	1963		1569		1008		593		2047
22	Middle test section wall temp	311		241		138		84		1528
23	(Mean of end temps) − (HVT temp)	152		42		14		−3		109
24	(Mean of end temps) − (MHVT temp)	12		−7		−14		−9		
25	(MHVT) − (HVT) = [(Mean of ends) − (HVT)] − [(Mean of ends) − (MHVT)] = (23) − (24)	140		49		28		6		109
26	(MHVT) − (No. 28 ga TC)	108		46		16		1		
27	(No. 28-ga TC) − (No. 22-ga TC)	54		28		11		3		
28	(No. 22-ga TC) − (No. 14-ga TC)	29		16		25		19		41
29	(No. 14-ga TC) − (No. 8-ga TC)	59		24		15		6		38
30	(HVT temp) − (HVT rad. shield temp)	146		112		92		73		107
31	(MHVT temp) − (MHVT rad. shield temp)	13		14		13		8		

Notes: HVT denotes high-velocity thermocouples
MHVT denotes multiple-shield high-velocity thermocouples
TC denotes thermocouple
All temperatures are in °F

the platinum platinum-rhodium thermocouple. A $\frac{3}{4}$-in O. D. by $\frac{1}{2}$-in I. D. by 4 in long porcelain radiation shield was used. Fig. 4 shows the fire-end of this assembly. A 22-gage Chromel-Alumel thermocouple was embedded in the radiation shield as shown, with the junction at the inner surface in order to obtain shield temperatures.

HVT suction velocities were measured with a $\frac{5}{8}$-in diameter orifice in a $1\frac{1}{2}$-in line. Maximum "dead-end" suction was 24.4 in Hg.

A special multiple-shield high-velocity thermocouple was also used (hereafter designated MHVT). The construction is also shown in Fig. 4. It consists of a $1\frac{5}{8}$-in I. D. refractory tube packed with 5-mm (0.197-in) O. D. by 4-mm (0.157-in) I. D. tubes. These tubes decrease the radiation between the thermocouple junction and the colder walls of the shield.

Bare 28 B. & S. gage Chromel-Alumel thermocouples were used in this assembly. The middle thermocouple was used for the MHVT reading. A second thermocouple, termed the "shield thermocouple," was placed in the outer tube-shield as shown, in order to obtain a measure of the temperature distribution across the tube-shields. As gas contamination was not a serious factor with the Chromel-Alumel thermocouples, it was not necessary to protect them against the action of the gases.

Table 1. Summary of Data of Laboratory Test Series 1 to 4 Using Middle Test Section.

(Results as given in lines 21 to 25 are plotted in Fig. 5)

	2 Test Section Air-Cooled								3 Transite Walls in Test Section with Cooling Coil						4 Transite Walls in Test Section		
	5-25-39		5-24-39		5-23-39		5-22-39		5-9-39		5-9-39		5-2-39		4-27-39	4-28-39	4-28-39
	1:00 PM	10:30 AM	10:35 AM	12:50 PM	1:00 PM	12:25 PM	3:10 PM	2:30 PM	3:43 PM	4:20 PM	3:00 PM	2:25 PM	1:15 PM	11:20 AM	1:34 PM	2:33 PM	10:23 AM
	1657	1631	1657	1637	1033	1031	583	605	2245	2188	1692	1660	1006	656	1685	1012	657
	1609	1584	1603	1588	998	994	563	588	2192	2139	1652	1633	993	646	1615	998	650
	1524	1503	1524	1513	969	970	556	584	2180	2130	1630	1610	970	630	1600	990	640
	1555	1528	1550	1534	980	981	562	588	2180	2136	1633	1618	982	640	1617	1000	647
	1568	1538	1575	1553	985	990	567	592	2194	2141	1640	1623	989	647	1623	1000	647
	1587	1556	1579	1561	993	995	569	594	2224	2170	1667	1650	989	647	1633	1002	652
	1602		1625		1010		577		2223		1681		1000	653	1646	1005	654
		1603		1617		1005		599		2169		1654					
	1633	1607	1630	1612	1015	1012	573	596	2218	2164	1672	1647	1000	651	1650	1005	654
MHVT not taken	31	4	5	−5	5	7	−4	−3	−5	−5	−9	−7	0	−2	4	0	0
	984	1033	1162	1181	659	664	311	325	2089	2054	1537	1518	877	552	1540	951	596
		570		431		341		274		115		136					
	1498	1580	1525	1606	958	1002	552	597	2175	2160	1618	1647	952	618			
												1589			1590		
	365	79.8	404	96	197	63.3	154	44	353	76.2	348	69.4	198.5	138.4	314	174.5	145.8
	14620	5340	15100	6090	13350	5950	14900	5720	12950	4000	12750	4430	14430	13760	15800.	13300	14320
	1588		1614		1011		581		2223		1685		1039	656	1694	1020	670
	976		1151		659		285		2089		1536		906	541	1590	968	610
	35		7		9		−6		−5		−12		0	−5	4	1	2
	2		−3		10		−3		−8		−8						
	33		10		−1		−3		3		−4						
	48		56		8		8		3		6		*10	*8	*15	*4	*3
	19		8		6		2		26		22		1	0	5	2	5
	5		21		9		3		6		4		9	6	6	2	1
	28		21		9		4		4		9		13	12	17	11	6
	102		101		55		32		44		63		48	39			
	27		11		4		2		9		9						

*(HVT) — (No. 28-gage TC) used on these readings

Test Procedure and Results

The following test series were run:

1. Middle-section walls water-cooled to obtain low wall temperatures, and gas temperatures at 2200°, 1600°, 1000° and 600 °F respectively.
2. Middle-section walls air-cooled to obtain intermediate wall temperatures, and gas temperatures at 2200°, 1600°, 1000° and 600 °F respectively.
3. Middle section constructed with Transite walls enveloped by a spiral copper cooling-coil through which water was circulated. The purpose of this construction was to obtain moderately high wall temperatures. The gas temperatures were 2200°, 1600°, 1000° and 600 °F respectively.
4. Middle section constructed with non-water-cooled Transite walls to obtain high wall temperatures, with gas temperatures at 2200°, 1600°, 1000° and 600 °F respectively.
5. Walls heated to the same temperature as the gas temperature at 2200°, 1500° and 1000 °F. These tests were run with the HVT inserted in the top section of the duct, instead of the middle test section, so that an electrically heated middle test section would not have to be constructed.
6. Walls at a temperature above the gas temperature to prove that the HVT temperature was below that of the bare thermocouples under these conditions.

On test series 6 no attempt was made to obtain high accuracy, as it was necessary to limit the scope of the investigation. This condition is not as frequently encountered in general engineering practice as is the condition with wall temperature cooler than gas temperature. Theory would indicate that errors involved with wall temperatures hotter than gas temperature are similar, but opposite in direction, to those involved with wall temperatures colder than gas temperature.

Sample data of individual runs for test series 1 to 4 are given in Table 1. A sample calculation for gas velocity and mass flow past the thermocouple hot junction is given in Appendix 1. All runs in each test of these series have also been averaged. The results are given in the lower part of Table 1. Gas temperatures given for top and bottom sections are the averages for all thermocouples at each location. The wall temperature of the test chamber is taken as the average of the four wall thermocouples.

Data for an additional run of test series 4 and data for test series 5 and 6 are given in Table 2. These data were taken in the top temperature-measuring section.

Table 2. Summary of Data of Laboratory Test Series 4 (Continued) to 6, Using Top Temperature-Measuring Section.

1	Test series	4 additional test		5			6
2	Kind of test	Walls not heated		Walls heated to gas temperature			Walls heated above gas temp
3	Date	6-1-39		6-1-39	5-19-39	5-23-39	5-25-39
4	Time	3:40 PM	3:50 PM	4:30 PM	2:45 PM	4:10 PM	4:15 PM
5	Wall temp (upper section)	2162 °F	2175 °F	2128 °F	1497 °F	1032 °F	1172 °F
6	HVT temp	2262	....	2130	1504	1034	600
7	MHVT temp	....	2266	....	....	....	....
8	Temp bare 22-ga thermocouple	2202	2205	2131	1503	1030	676
9	HVT−(22-ga temp)	60	....	−1	1	4	−76
10	MHVT−(22-ga temp)	....	61	....	....	....	
11	Radiation-shield temp	2200	2246	2133	1495	1032	743

It was first intended to use the mean of bottom- and top-section gas temperatures as the true gas temperature in the middle box to be compared with the HVT temperatures. This would be sufficiently accurate for the purpose, provided that the gas temperature drop across the middle or test section was not excessive. Experience demonstrated, however, that the relation between the mean temperature and the HVT temperature varied somewhat in different tests even when all conditions seemed identical. At times the HVT read even slightly above the mean temperature. This was probably due to stratification of flue gas in the duct. It was, therefore, decided to use the MHVT thermocouple as the standard. The MHVT never read more than 12 °F below the mean temperature or 14 °F above the mean temperature, and hence may be considered to be essentially equivalent to the mean temperature.

Since the MHVT and HVT thermocouple assemblies could not be used simultaneously in the apparatus, they could not be compared directly. Instead, the readings of each were compared with the mean temperature and thus they were indirectly compared with each other.

Fig. 5 summarizes the data contained in Tables 1 and 2. Test points are marked with the corresponding middle-section wall temperatures. These curves can be regarded as correction curves for the HVT only if the HVT is used in a four-inch-square duct under the conditions which governed these experiments.

Shield temperatures were taken in nearly all HVT test runs. Due to conduction along the thermocouple leads there was probably some error in these readings. However, there is a rough relationship between the error in the HVT readings and the difference between HVT and radiation-shield readings. Fig. 6 indicates this relationship.

From the data of Table 1 it is evident that the shield and gas temperatures have more nearly the same value for the MHVT as compared to the HVT.

The rings of small tubes give the same effect as would be obtained by using several concentric radiation shields with gas aspirated through the annular spaces. Thus the accuracy of the instrument is much improved.

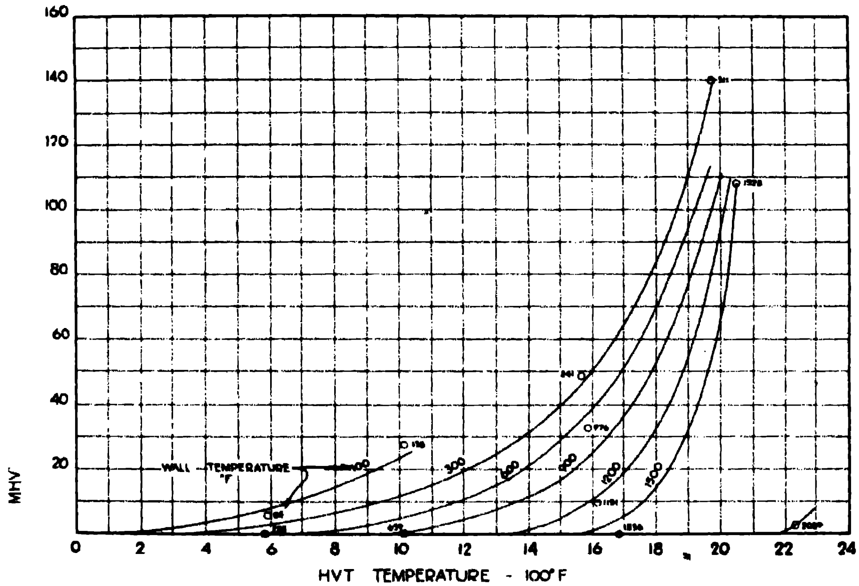


FIG. 5. Difference between readings of high-velocity thermocouple (HVT) and multiple-shield high-velocity thermocouple (MHVT) for various HVT temperatures (applicable only for a four-inch-square duct).

True Gas Temperature

As discussed in the preceding section, it had been the original intention to take as "true gas temperature" the arithmetic mean temperature of the bottom and top temperature-measuring sections. Due to gas stratification, it later became evident that the readings of the multiple-shield high-velocity thermocouple (MHVT) would furnish a better basis of comparison.

The question now arises: How close are the readings of the MHVT to the "true gas temperature?"

If the MHVT is compared to the average temperature of the bottom and top temperature-measuring sections taken as true gas temperature, the difference, by examination of Table 1, is plus or minus 14 °F, which is not large. The "true gas temperature" may also be estimated from another consideration. Theoretically the high-velocity thermocouple is subject to error as the radiation shield does not fully reach gas temperature. The more radiation shields that are used, the more closely the innermost radiation shield will approach gas temperature and the more accurate the reading.

If the MHVT temperature and the temperature of the MHVT shield are the same, theory indicates that there is no radiant-heat exchange and that the "true gas temperature" is actually being measured. The theory of radiation shields has been given by various investigators such as Schack[4] and will not be detailed here.

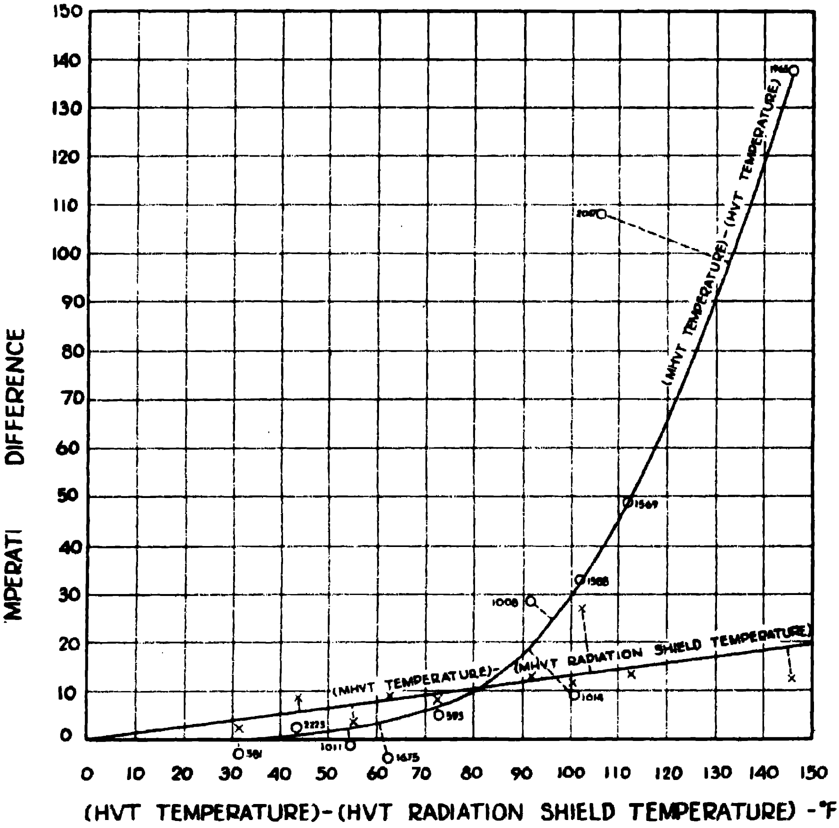


Fig. 6. Difference between readings of high-velocity thermocouple (HVT) and multiple-shield high-velocity thermocouple (MHVT) temperatures as a function of HVT shield temperature (Numbers beside data points correspond to HVT temperatures).

As shown by data plotted in Fig. 6, the difference between the thermocouple and the radiation-shield temperature was much smaller for the MHVT than for the HVT (20 °F for the MHVT corresponds to 150 °F for the HVT at high temperatures). Therefore, the MHVT should read much closer to the true gas temperature than the HVT temperature reads to the MHVT temperature.

Discussion of Results

The amount of error present in high-velocity thermocouple determinations as shown by the plotted results of Fig. 5 is appreciable. However, gas temperatures are generally measured in ducts of a larger size than the four-inch-square test duct. It would be expected that the error would be less in the larger ducts so that the data of Fig. 5 probably represents the maximum probable error. In steam boilers where ducts many feet wide are encountered, the error is somewhat less.

The data check in every detail the theory of the high-velocity thermocouple. Theory would indicate that the multiple-shield high-velocity thermocouple reads essentially true gas temperature and that the high-velocity thermocouple reads a lower temperature, with bare thermocouples reading still lower temperature.

Considering again the data of 5-31-39 given in Table 1, the following results are obtained.

	°F
Estimated true gas temperature	2105
MHVT temperature	2103
MHVT shield temperature	2090
Bare 28-gage thermocouple (0.013 in dia.)	1995
HVT temperature	1963
Bare 22-gage thermocouple (0.025 in dia.)	1951
Bare 14-gage thermocouple (0.064 in dia.)	1922
Bare 8-gage thermocouple (0.128 in dia.)	1863
HVT shield temperature	1817
Optical pyrometer (hot-wire) temperature	1607
Wall temperature	311

The foregoing data are graphically illustrated in Fig. 7 and indicate the errors possible in gas-temperature measurement. The values have been confirmed in magnitude by many hundreds of field determinations.

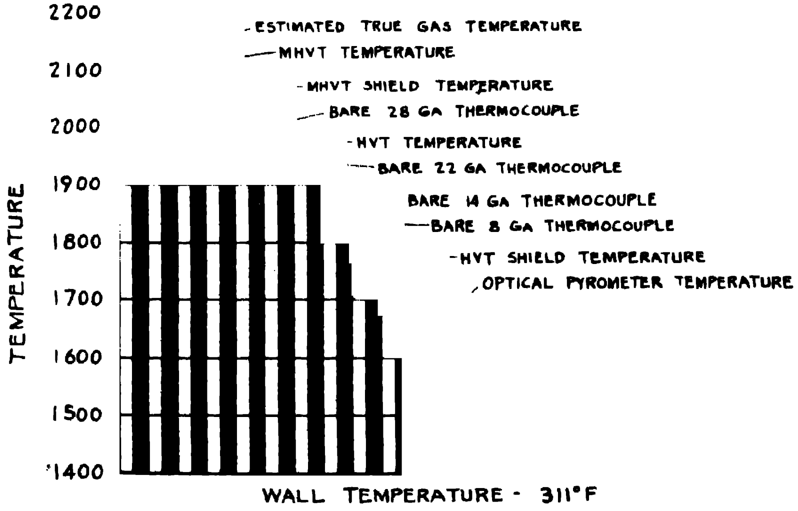


FIG. 7. Typical comparative readings of different types of thermocouples in a four-inch-square duct. Test of 5-31-39. HVT denotes single-shield high-velocity thermocouple. MHVT denotes multiple-shield high-velocity thermocouple.

It is apparent that any temperatures given to support experimental data should have the method of temperature measurement specified.

Additional confirmation of high-velocity thermocouple theory is given by the data of Table 2. When the HVT and the wall temperatures are the same, bare thermocouples likewise give the same reading. When the HVT gas temperature is above the wall temperature, the bare thermocouple reading is below the HVT temperature. When the HVT gas temperature is below the wall temperature the bare thermocouple reading is higher than the HVT temperature.

In general, it is recommended that, when wall temperatures differ appreciably from gas temperatures, an HVT or an MHVT be used. Where slag-bearing gases are not encountered, gas temperatures should be measured by multiple-shield high-velocity thermocouples. Where slag prohibits practical use of the MHVT, the HVT high-velocity thermocouple should be used. A correction from HVT to MHVT may be established by special tests.

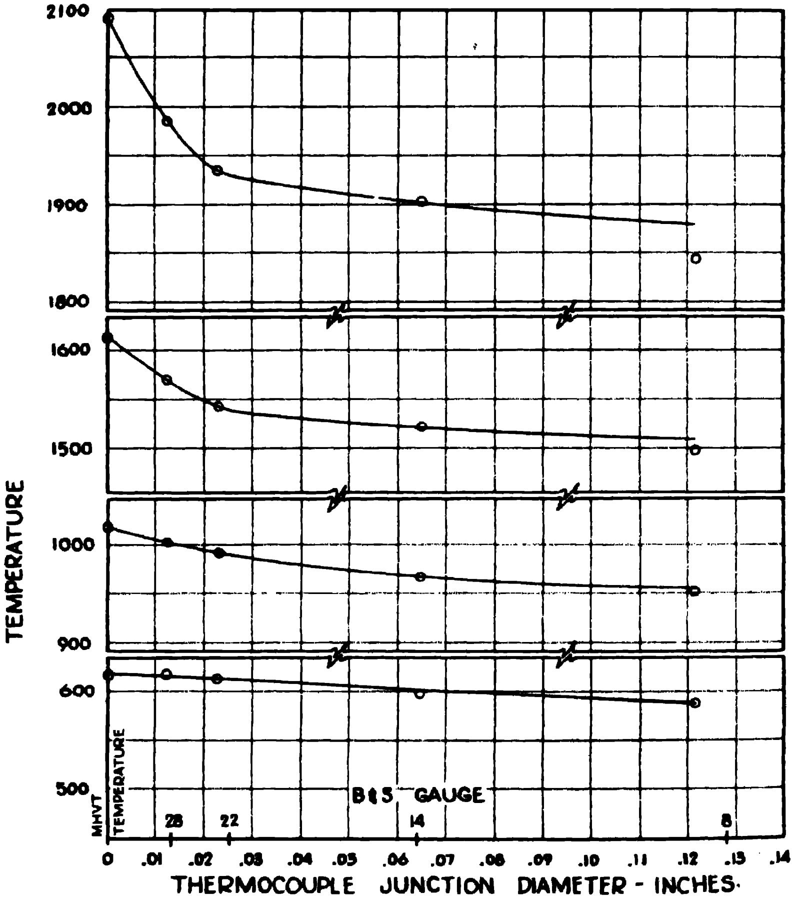


FIG. 8. Temperature indicated by bare thermocouples plotted vs. thermocouple diameter (actual measured diameters).

Small-diameter bare thermocouples are very fragile, so that 28-gage wire is most difficult to use in a bare thermocouple installation. In slag-bearing gases its use is impractical, as the wire collects slag and increases its diameter. At high temperatures, where platinum thermocouple wire must be used, the small exposed bare wire rapidly loses calibration because of gas contamination. At higher gas temperatures, where errors become appreciable, it is generally necessary to use water-cooled holding tubes, so that the high-velocity thermocouple is almost as easy to use as bare thermocouple equipment. The use of bare thermocouples is, therefore, not desirable at higher gas temperatures.

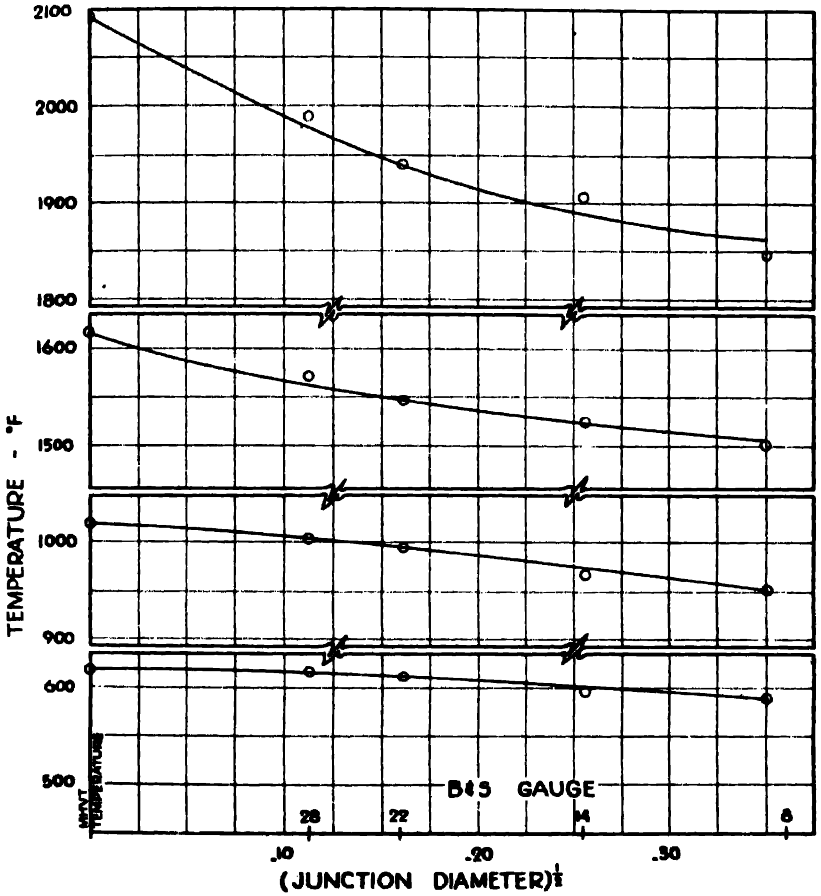


Fig. 9. Temperature indicated by bare thermocouples plotted vs. square root of thermocouple diameter.

At the lower temperatures, where gas temperatures approach wall temperatures, the errors (due mostly to radiation) are not large and the bare thermocouple has a distinct field of use.

As a point of interest, optical-pyrometer temperatures were also taken. Frequently an optical-pyrometer temperature could not be obtained because the reading was below scale. When obtained, the readings were low compared to thermocouple readings. Due to the small duct width (4 inches) and to the clear, non-luminous gas, an optical pyrometer used under such conditions tends to read a temperature between the wall temperature and the gas temperature. The optical pyrometer, *therefore, could not be expected to read very accurately in the apparatus used for the present tests. In large enclosures, where the walls approach gas temperatures and the gases are luminous, the optical pyrometer would read close to the true gas temperature.*

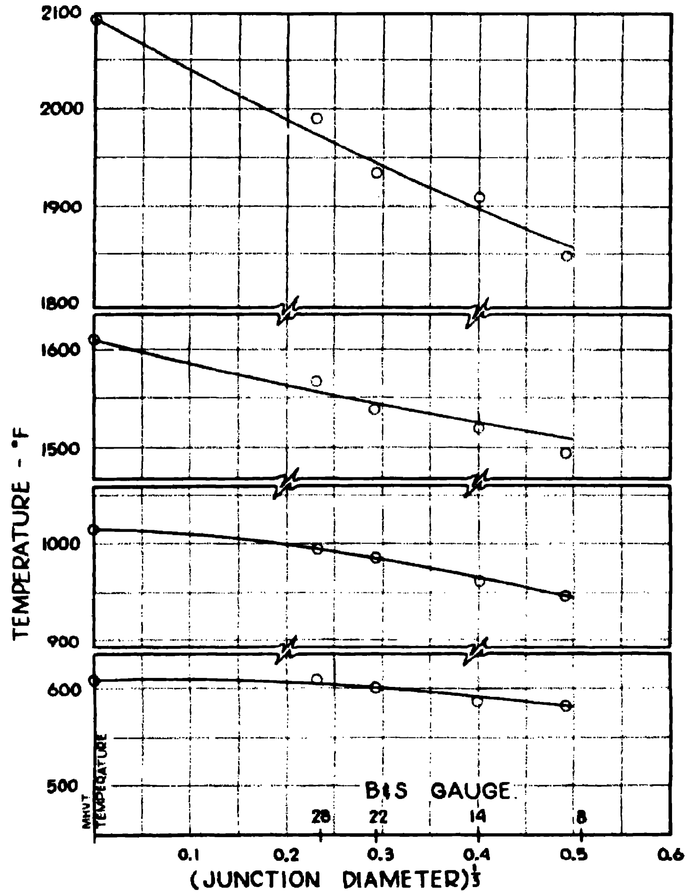


FIG. 10. Temperature indicated by bare thermocouple plotted vs. cube root of thermocouple diameter.

Comparison of Multiple-shield High-velocity Thermocouple (MHVT) Readings with Small-gage Bare-wire Thermocouples and Extrapolation of Bare-wire Thermocouple Results to Zero Diameter

The MHVT and HVT thermocouples were also compared on the various tests, with readings of bare-wire thermocouples of different diameters. The bare-wire Chromel-Alumel thermocouples were butt-welded and the junction diameters were individually measured.

Numerous attempts have been made by various investigators to obtain true gas temperatures by the use of three or more thermocouples of different junction diameters, by means of the extrapolation of such results to zero diameter thermocouple.

Fig. 8 shows four curves of this type. Each of the curves represents average results for one series of tests. The MHVT temperature has been plotted at zero diameter of thermocouple junction. It is probable that the true temperature is actually slightly higher than this MHVT temperature, since the bare-wire thermocouples were about 1 inch below the MHVT in the duct, *i.e.*, on the hot side. The curves indicate the difficulty of extrapolating to zero diameter. The probable error due to the rapidly changing slope of the curves near zero diameter is quite large, especially at high temperature differences between walls and gas.

If the temperature readings of the various thermocouples are plotted against a fractional power of the thermocouple diameters, the curves become somewhat straighter. Figs. 9 and 10 show plots, using square and cube roots respectively, of thermocouple diameters. Even these are not very satisfactory. The lower the fractional power the further the curve must be extrapolated. Thus on Fig. 8 the extrapolated portion is about one-quarter as long as the established length of curve, whereas in Fig. 10, where the cube root is plotted, the extrapolated length is approximately equal to the determined portion.

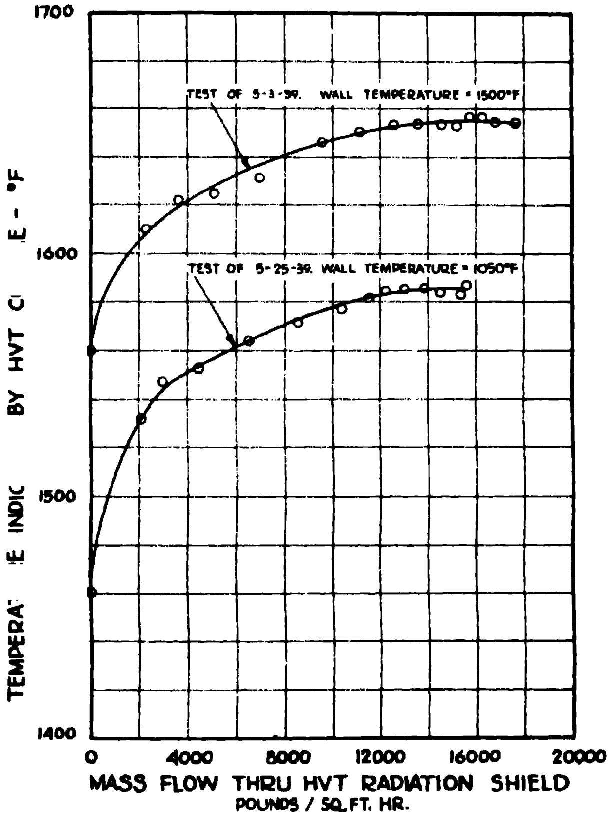


FIG. 11.
Influence of gas-flow rate through high-velocity thermocouple on temperature indication.

If the junction diameters are plotted on a log scale, an approximately straight line is obtained. However, such a curve cannot be extrapolated to zero diameter. In any event, the determination of gas temperatures by extrapolation of bare thermocouple readings of different diameters is not satisfactory. In the determination of gas temperatures in pulverized-coal-fired installations, the slagging of the thermocouples seriously affects the readings. Also it should be noted that very constant temperature conditions are necessary for this work, since small-diameter thermocouples respond much more quickly to temperature changes than do large-diameter thermocouples.

For gas temperatures above the useful range of Chromel-Alumel thermocouples (2500 °F) it is necessary to use platinum thermocouples. The use of platinum thermocouples without means of protection from gas contamination is not advisable; hence the determination of gas temperatures by the method of extrapolation of bare thermocouple readings of different diameters is impractical above 2500 °F.

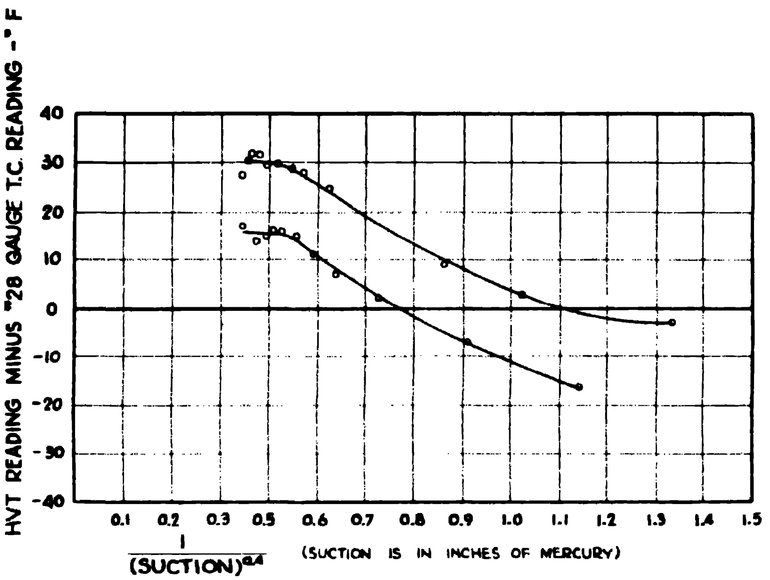


FIG. 12. Readings of high-velocity thermocouple plotted vs. the reciprocal of the 0.4 power of suction.

Effects of Aspiration Velocity on High-velocity Thermocouple Reading

For all tests the gas velocity of the HVT was maintained at such a point that an increase in velocity produced no noticeable rise in HVT temperature. Typical curves of temperature indicated by HVT vs. mass velocity of gas past hot junction are shown in Fig. 11.

Other investigators[5] have reported that a plot of (HVT temperature) – (bare thermocouple temperature) against $1/(\text{suction})^{0.4}$ gives a straight line which may be extrapolated to infinite velocity to obtain true temperature. Fig. 12 shows data of Fig. 11 plotted in this manner. Because of slight variations in firing rate of the furnace which heated the gas used in the test equipment, momentary variations in absolute temperature occurred. It was reasoned that the relation between HVT and bare 28-gage thermocouple would be nearly independent of this variation; hence in Fig. 12, (HVT temperature) – (bare 28-gage thermocouple temperature) instead of HVT temperature has been plotted against $1/(\text{suction})^{0.4}$. In Fig. 12 the plots obtained are not straight lines so that the extrapolation to infinite velocity

$[1/(\text{suction})^{0.4} = 0]$ would appear to be difficult. Moreover, there is a "break" in the curve at a certain value which may indicate a critical velocity. This matter was not pursued further, as the time required to take the number of test readings needed to establish a single gas temperature was objectionable.

The possible existance of this critical velocity, more apparent in Fig. 12 than in Fig. 11, may explain why, in practice, the temperature indication of the HVT does not increase beyond a certain mass flow (gas velocity past thermocouple junction), and thus why the HVT reading does not approach higher values.

Effect of Protection-tube Diameter on High-velocity Thermocouple Accuracy

When platinum, platinum-rhodium thermocouples are used to measure gas temperatures, it is necessary to protect the thermocouple from contamination by the flue gas. The effective thermocouple diameter then, of course, becomes the outside diameter of the protection tube. A few tests were run to determine the effect on HVT accuracy of varying the diameter of this protection tube. Two sizes of protection tubes were used, one 5 mm O. D. (about .198 in), the other $\frac{1}{4}$ in. O. D. Examples of typical runs appear in Table 3. Summarized results are given in Table 4. The temperature indicated with the smaller diameter protection-tube appears to be close to the mean temperature. Thus, although this factor is not of great importance under conditions likely to be met in actual temperature surveys, it would seem advisable to use protection tubes of the smallest possible diameter.

Table 3. Effect of Protection-tube Diameter on High-velocity Thermocouple Accuracy.

(Typical Test Runs.)

(For Summary See Table 4.)

1	Date	5-25-39		5-19-39	
2	Time	12:50 PM	2:30 PM	2:00 PM	11:15 AM
3	Gas temp entering test section	1662 °F	1630 °F	1628 °F	1635 °F
4	Gas temp leaving test section	1610	1587	1553	1550
5	Middle section wall temp	965	965	226	234
6	HVT temp (in middle section)	1602	1565	1558	1542
7	Mean of end temps	1636	1608	1590	1592
8	Mean of ends – HVT temp	34	43	32	50
9	Radiation-shield temp	1498	1473	1409	1425
10	Protection-tube diameter	0.198"OD	0.25"OD	.198"OD	.25"OD

Table 4. Effect of Protection-tube Diameter on High-velocity Thermocouple Accuracy.

(Summary of Test Data.)

Date	5-25-39	5-19-39
HVT temp	1614 °F	1567 °F
Mean temp – HVT (0.198" tube)	35	32
Mean temp – HVT (0.25" tube)	43	50
Mean temp – MHVT	2	– 14
HVT (.198" tube)—HVT (.25" tube)	8	18
MHVT – (middle-wall temp)	579	1402

Steel Radiation Shield

A few tests were made with a steel radiation shield instead of the customary porcelain shield. Internal and external diameters were practically identical with those of the porcelain shield.

It was expected that the better thermal conductivity of the metal shield would decrease the temperature gradient from inner to outer surface of the shield and that the HVT temperature might then be lower than that with the porcelain shield. This was found not to be the case. Shield and HVT temperatures were found to be practically identical regardless of whether the steel or the porcelain shield was used. Sample data are shown in Table 5.

Table 5. Tests of Special Radiation Shield Compared to Porcelain Radiation Shield.

1	Date	5-25-39		5-23-39		5-22-39	
2	Time	12:50 PM	10:55 AM	1:05 PM	10:50 AM	2:50 PM	4:00 PM
3	Radiation shield material	Porcelain °F	Steel °F	Porcelain °F	Steel °F	Porcelain °F	Steel °F
4	Gas temp entering test section	1662	1661	1033	1042	572	598
5	Gas temp leaving test section	1610	1613	998	1002	554	581
6	Middle section wall temp	965	965	659	646	310	301
7	HVT temp (in middle section)	1602	1612	1010	1017	568	595
8	Mean of end temps	1636	1637	1015	1022	563	590
9	Mean of ends – HVT temp	34	25	5	5	– 5	– 5
10	Radiation shield temp	1498	1508	958	965	544	561

It is perhaps not strictly accurate to compare these shield temperatures, since with the metal shield, the shield thermocouple was peened in the outer surface, while with the porcelain shield the welded junction of the thermocouple was placed flush with the inner face of the shield.

Although a metal shield should prove more serviceable at low temperatures, it would not be practicable at the higher temperatures reached in a steam-boiler furnace.

Effect of Radiation-shield Diameter on High-velocity Thermocouple Accuracy

A short test was run at 1600 °F with water-cooled walls to determine effect of radiation-shield inner diameter on the accuracy of the HVT. The results using the usual $\frac{1}{2}$-inch I. D. porcelain radiation shield were compared with those using a $\frac{15}{16}$-inch I. D. porcelain radiation shield. The same porcelain protection tube was used in each test. Table 6 shows typical results. No appreciable difference in accuracy was found. The foregoing two sizes of radiation shields appear equally satisfactory.

Table 6. Effect of Radiation Shield Diameter (Porcelain Radiation Shields Used).

1	Date	5-26-39	
2	Time	10:30 AM	1:15 PM
3	Inside dia of radiation shield	0.5"	0.94"
4	Gas temp entering test section	1661 °F	1644 °F
5	Gas temp leaving test section	1595	1572
6	Middle section wall temp	240	247
7	HVT temp (in middle section)	1575	1554
8	Mean of end temps	1628	1608
9	Mean of ends – HVT temp	53	54
10	Radiation shield temp	1462	1454

Effect of Cement Used to Close Ends of Protection Tube

When using single-bore protection tubes, the fire end of the protection tube must be closed with plastic refractory cement in order to prevent gas contamination of the thermocouple junction. Two such cements were tried to determine their suitability for such use.

It was found that when the junction of a platinum thermocouple was coated with "Carbofrax" cement and placed in a laboratory furnace at 2500 to 2600 °F, the thermocouple broke in a few minutes, undoubtedly due to the action of the cement. A thermocouple coated with "Sauereisen" porcelain cement under the same conditions did not break during three hours' exposure to the same temperature, and showed no change in calibration. For this and other reasons the "Sauereisen" cement was used for protection-tube end-closure.

APPENDIX 1

Sample Calculation for Gas Velocities and Mass Flow Past Thermocouple Hot Junction

Derivation of Formulas

From Marks, "Mechanical Engineers' Handbook," Third Edition, page 264.

$$V = C_0 \sqrt{\frac{2gH}{1-\left(\frac{A}{A_1}\right)^2}} \tag{1}$$

V = velocity of gas through orifice (ft/sec).
C_0 = constant, (chosen as 0.60).
A = area of orifice = .3068 sq in.
A_1 = area of pipe containing orifice.
H = orifice differential (ft of flowing media).

$$H = \frac{62.2}{12}\left(\frac{1}{.07355} \times \frac{(460+t)}{540} \times \frac{29.93}{P}\right)h \tag{2}$$

t = temperature of gas at orifice (°F).
P = absolute pressure of gas at orifice (inches Hg).
.07355 = density of flue gas at 80 °F and 29.93 inches Hg.
h = differential across orifice (inches of water).
$T = (t + 460) = °R = °F$ absolute. (3)

$$H = 3.90\,\frac{Th}{P} \tag{4}$$

$$V = .60\sqrt{\frac{64.4H}{.997}} \tag{5}$$

$$= 4.82\sqrt{H} \tag{6}$$

Q = volume of gas through orifice/sec = AV (7)

$$= \frac{.307}{144}\,V \tag{8}$$

$$= .01056\sqrt{H} \text{ cu ft/sec} \tag{9}$$

$$V_0 = V \times \frac{A}{A_2} \times \frac{T_1}{T} \tag{10}$$

V_0 = velocity of gas through radiation shield, around thermocouple (ft/sec).
A_2 = cross-sectional area of gas passage in radiation shield (sq in).
T_1 = HVT temperature (°R).

A_2 = 0.167 sq in, using .198-in O. D. protection tube and 0.5-in I. D. shield.

= 0.148 sq in, using .25-in O. D. protection tube and 0.5-in I. D. shield.

= 0.533 sq in, using MHVT protection tube and 0.5-in I. D. shield.

A = orifice area = .307 sq in.

$$V_0 = 4.82\sqrt{H} \times \frac{.307}{.167} \times \frac{T_1}{T} \tag{11}$$

$$= 8.9\frac{T_1}{T}\sqrt{H} \text{ for 0.198-in O.D. protection tube, 0.5-in I.D. radiation shield} \tag{12}$$

$$V_0 = 4.82\sqrt{H} \times \frac{.307}{.148} \times \frac{T_1}{T} \tag{13}$$

$$= 10.0\frac{T_1}{T}\sqrt{H} \text{ for 0.25-in O.D. protection tube, 0.5-in I.D. radiation shield} \tag{14}$$

$$V_0 = 4.82\sqrt{H} \times \frac{.307}{.533} \times \frac{T_1}{T} \tag{15}$$

$$= 2.775\frac{T_1}{T}\sqrt{H} \text{ for multiple-tube HVT} \tag{16}$$

G = "mass" flow through radiation shield (lb/sq ft hr).

w = weight density of gas at hot junction temperature (°F).

$A_2/144$ = free-flow area inside radiation shield (sq ft).

$$G = Q\frac{w}{\frac{A_2}{144}}3600 \tag{17}$$

$$= Q\frac{.07355 \times \frac{540}{460+t} \times \frac{P}{29.93} \times 3600}{\frac{A_2}{144}} \tag{18}$$

Writing gas density in terms of $\left(\frac{h}{H}\right)$ from Equation (2).

$$G = Q\frac{5.18 \times \frac{h}{H} \times 144 \times 3600}{A_2} \tag{19}$$

Substituting value of Q from Equation (9)

$$G = \frac{5.18 \times 0.01056\sqrt{H} \times \frac{h}{H} \times 144 \times 3600}{A_2} \tag{20}$$

$$= 170{,}000\frac{h}{\sqrt{H}} \text{ for 0.198-in O.D. protection tube, 0.5-in radiation shield} \tag{21}$$

$$= 192{,}000\frac{h}{\sqrt{H}} \text{ for 0.25-in O.D. protection tube, 0.5-in radiation shield} \tag{22}$$

$$= 53{,}200\frac{h}{\sqrt{H}} \text{ for MHVT} \tag{23}$$

Example

Date 5-26-39

10:40 A. M. reading with 0.5-in I. D. radiation shield and .198-in O. D. protection tube.

HVT temperature 1566 °F; orifice temperature, 80 °F; orifice differential = .63 inch water.

Absolute pressure at orifice = 19.8 inch Hg.

$$
\begin{aligned}
H &= 3.90\frac{Th}{P} = 3.90\frac{540 \times .63}{19.8} \\
&= 67.1 \\
V_0 &= 8.9\frac{T_1}{T}\sqrt{H} \\
&= 8.9 \times \frac{2026}{540}\sqrt{67.1} \\
&= 275 \text{ ft/sec velocity through HVT shield.}
\end{aligned}
$$

$$
\begin{aligned}
\text{Mass flow through shield} = G &= 170{,}000\frac{h}{\sqrt{H}} \\
&= 170{,}000\frac{0.63}{\sqrt{67.1}} = 13{,}000 \text{ lb/sq ft hour}
\end{aligned}
$$

Discussion

Mr. L. C. Sheldon*: Mr. Mullikin should be highly commended for his very interesting and instructive paper on "Gas-Temperature Measurement," which gives the recent developments in methods of measuring boiler gas temperatures. He points out the good features and the possible errors which may be encountered when using these different methods. The measurement of these gas temperatures has always been difficult and the accuracy has been somewhat uncertain. What is needed for this purpose is an instrument of measurement which is simple, reliable and accurate, and which can be left in flue gases continuously and still give accurate readings. I have not heard that anyone has accomplished all this, but believe that Mr. Mullikin has gone quite a long way in this direction by the use of high-velocity and multiple-shield high-velocity thermocouples. As he points out, by the use of such couples the temperature measurements can be made with a high degree of accuracy.

In the paper "Accuracy Tests of the High Velocity Thermocouple" he and W. J. Osborn show that with the multiple-shield high-velocity couples results can be obtained within 10 or 12 degrees of the correct value. When measuring dirty gases, such as are encountered in pulverized coal furnaces, the couples slag over quite quickly and so can be inserted in the flue gas space only during the short time it takes to get a reading.

In my opinion both of these papers are very valuable and instructive.

Mr. H. E. White†: Full utilization of the authors' work should lead to important progress. They have attacked a problem which has been under investigation during several decades, both in this country and abroad. The complete review of the literature will be particularly convenient for those entering the field. The authors have confirmed the high accuracy of the multi-shielded high-velocity thermocouple and have demonstrated its value as a basis of comparison for other instruments under actual operating conditions, where the gases are dust-free.

The recommendation that the MHVT should be used for gases free of slag, as for gas- or oil-fired installations, should lead to much more precise determination of heat absorption rates in the component sections of large steam boilers under conditions of commercial operation. For such applications the MHVT described will permit precise temperature observations during extended periods, yielding significant average values where fluctuations commonly occur.

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It is important, also, that it was found possible to measure accurately high gas temperatures in commercial boilers fired with pulverized coal and hence, in industrial furnaces with dust-laden gases, even though the existing MHVT equipment is inconvenient for this application.

It should be noted, in connection with the discussion of exposed thermocouples of graduated sizes, that although this method is considered by the authors as unsatisfactory for general use, the results obtained in their laboratory furnace, under test conditions, appear to be well correlated.

Not the least important conclusion is that, wherever high-temperature observations are reported, the method of observation must be stated, to permit precise interpretation of the results. It might be added that the method of correction should be stated also.

The development of modern steam boilers and certain types of industrial furnaces has brought the subject of gas temperature measurement to attention as an important component problem in the further improvement of designs. Hence, rather full discussion from that point of view may be warranted.

The detailed discussion which follows concerns the high-velocity thermocouple, particularly as related to observations in pulverized-coal-fired steam boilers and furnaces.

While the simple HVT is shown to be more nearly correct than other instruments commonly used with dust-laden gases, the authors reach the important conclusion that it may give results containing appreciable errors. This confirms the conclusions of other investigators. For some important applications, even under ordinary conditions of operation of modern commercial boilers, the magnitude of the errors may be excessive.

Since the simple high-velocity thermocouple is recommended for use where the high-temperature gases may be laden with dust or molten slag particles, three significant questions are suggested in connection with pulverized-coal-fired boilers:

(1) What is the maximum error of the present high-velocity thermocouple which may be expected in modern steam boilers other than in the furnace?

(2) What limitations must be observed in applying a single correction curve to the observations?

(3) What possible means might be considered for improving methods of observation for pulverized-coal boiler units?

(1) Maximum Errors of Observations of the HVT with Steam Boilers

The curve labeled "MHVT" in Fig. 27 (page 800) indicates that the error obtained with the HVT in the furnace of a steam boiler may be approximately 100 °F at a temperature of 2300 °F. Since the curve represents the average for several installations, however, it would be expected that the average value of 100° might be exceeded in individual furnaces.

As this curve represents the error determined by observations in large furnaces, the effect of luminous flame may reduce the radiation effect of the "cold" water-wall tubes. In some cases water-wall tubes may be shielded by slag deposits of various thicknesses and surface temperatures. For these reasons it would be expected that, for locations other than in the furnace, the errors shown by the curve might be exceeded. For example, if the instrument were located at the gas outlet from the first bank of boiler tubes it might be almost completely surrounded by relatively "cold" surfaces; and just after the slag deposits had been removed from the boiler tubes the radiation error would be a maximum for the prevailing gas temperature. It will be noted from the "MHVT" curve mentioned above that at a gas temperature of 1800 °F an error of approximately 60 °F is reported. From these data it might be estimated roughly that, if the instrument were completely surrounded by bare tubes, observations on gas at temperatures of 2300 to 2400 °F might be 150° too low.

Since the radiation error of the HVT arises in part from the same causes as for the exposed couples, it would be expected to vary in a manner similar in some ways to that for a bare couple of No. 14 wire as reported in Fig. 27 (page 800). Although the errors for the HVT were observed only for locations in furnaces, the errors for exposed thermocouples were determined both for furnaces and also for "cavities," as shown in Fig. 27. The corresponding curves suggest a basis for estimating the comparative magnitude of error of a given HVT in different locations. Thus, in relation to a true temperature of 2400 °F, the error for an instrument in a "cavity" might be roughly 30 per cent greater than for one in the furnace; and an intertube location would give a greater error than either of the preceding locations. On this basis the error of the HVT might reach 140 °F at 2400 °F for individual cases.

This would appear to be approximately in agreement with the observations in the laboratory furnace as indicated in Fig. 5 (page 813) considering that the instruments under test were not completely surrounded by cooled surfaces.*

These rough estimates suggest that for locations other than in the furnace, the error of the HVT used by the authors might reach 150 °F at gas temperatures of 2300 to 2400 °F.

(2) Impracticability of Single Correction Curve for Precise Results

As pointed out by the author under the heading "Bare Thermocouple with Calculated Correction" (page 779), the amount of the radiation error will vary with many factors. These include the location of the instrument, the proportion of the surrounding surface which is cooled, the arrangement of the surfaces, the shielding characteristics of the flame, as well as its size and position, and the distribution and thickness of slag deposits; also, the nature of the slag with respect to the maximum temperature attainable at its surface before running on the furnace walls. These factors vary with the design of the boiler, the kind of coal in use, its ash characteristics, and even the fineness of grinding, as well as the rate of firing and the location of the instrument. It would seem impracticable, therefore, to use the single curve labeled "MHVT" in Fig. 27 (page 800) as a correction curve for the HVT where reliable and reasonably precise results are required. Obviously a correction curve determined for each individual instrument location would be preferable if conditions permitted obtaining it.

(3) Possible Improvement of Instrument for Dust-laden Gases

For certain purposes, temperature observations with an indeterminate error of the order observed would be undesirable; for example, the "sticky" temperature of floating ash particles may be critical in boiler operation, just as the operating temperatures of industrial furnaces may be. Another application mentioned by the authors is the determination of heat absorption rates in different portions of a boiler by computing the rate of heat loss from the combustion gases between selected cross-sections of the gas stream. It will be noted that here the result depends directly upon the difference of gas temperatures observed at two or more locations. Since one of the locations may be in the furnace, the error at that point may not be comparable with that at a later point in the gas stream. Correspondingly, the temperature differences would be in error by an undetermined amount which might be a large proportion of a temperature drop of a few hundred degrees.

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* Because of use of uncooled refractory tubes as screens on the two sides of enclosure, through which the combustion gases enter and leave.

Such cases emphasize the desirability of an instrument less troublesome with slag than the present MHVT and having an accuracy and reliability greater than the present single-shield HVT.

The precision of the multiple-shield type has been clearly demonstrated. The only important deterrent to its application to dust-laden gases is the inconvenience of slag accumulations. In some cases the advantage of the greater precision available may justify the use of the multi-shield type of instrument in spite of the inconvenience caused by rapid clogging. It is suggested, however, that further consideration might be given to possible modifications of instrument designs which would improve the accuracy of observation over that of the HVT without unduly increasing the rate of plugging.

It would seem desirable, therefore, to consider means of:

(a) Improving the precision of the simple HVT without greatly increasing the inconvenience of ash and slag accumulation within the instrument.

Or, conversely, to:

(b) Modify the design of the multiple-shield, high velocity thermocouple so as to reduce the inconvenience of dust and slag accumulations.

Reply

The authors thank Mr. Sheldon for his comments, and are in full agreement with Mr. White's remarks concerning the theory of the HVT error.

In actual boiler test work there has been considerable difficulty in noting the effect on HVT readings of the variables mentioned by Mr. White. Combustion is a dynamic process and flue gas temperatures resulting therefrom vary from moment to moment. Because of this, individual or instantaneous readings may be confusing. The temperature lags of the MHVT and HVT are inherently different and also depend on the amount of slag on the insulators.

Because of this, MHVT minus HVT differences obtained at the same location in the gas passes on a steam-boiler unit differ from minute to minute, from point to point and particularly from day to day. Similar differences are noted at corresponding locations on different boiler units. In addition to variations in local combustion rates these MHVT-HVT differences are undoubtedly due to different amounts of slag on adjacent surfaces, gas luminosity, or other influences. Our efforts at correlation in this regard have not been very successful.

For a MHVT – HVT average difference of 100 °F individual readings may be plus or minus 30 or 40 °F from this value, but we have not been able to correlate this with any determinable operating factors to show when it will be plus or when it will be minus.

Similarly it has not as yet been possible to distinguish a difference in MHVT – HVT reading between a location at a furnace outlet and in a three- or four-foot-high cavity. Within practical limits the MHVT correction curve of Fig. 27 may be used for both furnaces and cavities between boiler tube banks as it has been established by data from both locations in various units.

Some typical data taken on a natural-gas-fired unit at one location at the furnace outlet is shown in Fig. 28 (p. 801). Two series of simultaneous MHVT, HVT and bare thermocouple readings were taken, the two series being taken one hour apart during which there was no observable difference in boiler condition or operation. It will be noted that at the same location the MHVT – HVT correction may be 90 °F on one test series and 135 °F on the second test series. These are typical data. To obtain average corrections at least five test series may be desirable. Due to thermocouple contamination and breakage so many observations are difficult to obtain with the MHVT. The average may be assumed correct but the reasons for deviation of individual readings from the average must be ascribed to the factors not at present determinable.

Due to extreme gas temperature gradients behind and between tubes the authors have been unable to determine any satisfactory intertube data (*i.e.*, data between tubes in a relatively close-spaced tube bank).

At the time of writing the maximum average MHVT-HVT difference at any location in the gas pass of the many steam boilers tested to date has not been above 140 °F. Individual readings used to obtain this average might have been plus or minus 40 °F from the value.

After the paper was written natural-gas-fired units have been tested and difficulty was encountered due to loss of calibration of the platinum thermocouple wire by gas contamination from some constituents of the flue gas. On this account, use of the MHVT for gas-fired units still presents considerable uncertainty.

The authors are still accumulating data from test work, involving the use of this equipment and endeavoring to improve the equipment. They are investigating other methods of gas temperature measurement as they may be suggested or developed from time to time. The authors have hopes of developing a method in the future of measuring gas temperature by utilizing the velocity of sound in the flue gas whose temperature is being measured.

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Report on the Institute of Fuel Symposium on Gas Temperature Measurement

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For some years past, practical engineers concerned in the use of high temperatures have found that attempts to increase the accuracy of heat-transfer calculations were likely to break down on account of the serious errors encountered in gas temperature measurement. Measurements with exposed thermocouples and even suction pyrometers, which had been quite naïvely accepted as giving a close measure of a gas temperature, were found to be liable to errors of ten per cent or more on the absolute temperature. Thus, measurements of temperature based upon bringing a test body into equilibrium with the gas were found to be likely to fail in the presence of radiating surfaces at a different temperature. On the other hand, measurements based on radiation were liable to serious error in the absence of a blackbody radiator.

A Joint Committee of British furnace builders and steel makers investigated this problem in 1938 and recommended that a symposium should be organized to promote an exchange of experiences between engineers and scientists.

The Council of the Institute of Fuel of Great Britain undertook to convene the Symposium and the organizing work was undertaken by Messrs. A. F. Webber and J. M. Ridgion of the British Iron and Steel Federation.

The Conference, which was held in London on December 2, 1938, was successful in the sense that it led to a better appreciation of the theoretical and practical difficulties of gas temperature measurement, but it cannot be said that any important innovations in technic were proposed in any of the papers. The following is a summary of the principal points of interest in the seventeen papers and the discussion, the whole of which has been published as a single volume in the Proceedings of the Institute of Fuel, from whose address at 53 Victoria Street, London, S. W. 1, copies are available.

I. Theory of Gas Temperature Measurement

The temperature of a system in thermodynamic equilibrium has a very clearly defined and precise meaning. On the other hand, there are very few, if any, cases in industrial practice where this equilibrium is attained, and the extension of the idea of temperature to cases of non-equilibrium requires considerable theoretical, as well as practical, investigation. An outline of such a theoretical investigation is given by Bennett and Pirani, who define a type of incomplete equilibrium, which they call *transflux equilibrium.*

Transflux equilibrium occurs in all cases where there is a flow of energy, either molecular or electromagnetic, maintained constant from a source such as a chemical reaction or the passage of an electric current to a sink of large heat capacity. When there is transflux equilibrium, the temperature of a gas not only may vary from point to point, but also may have more than one significance at any given point.

To give precision to this idea, Bennett and Pirani introduce the concept of an *energy flow trap,* defined as follows:

> "In the absence of thermal equilibrium, one or more of the various energy carriers may be isolated or partially isolated from the others, with the result that the equi-partition of energy between the different degrees of freedom will be prevented or delayed. In this case, each class of energy carriers is called an Energy Flow Trap."

Each energy flow trap, such as the kinetic energy of translation and the energy of electron excitation can have a different "temperature." * In this case, temperature means the temperature of an equilibrium enclosure in which that particular energy flow trap would have the same energy.

These ideas provide a basis upon which to classify the remaining papers of the Symposium. Thus, there is one paper which deals with the materials of thermocouples, *i.e.*, with the problem of measuring temperature in the case where its meaning is precise, and one or two others are concerned with the design of instruments and auxiliary apparatus.

Nearly all the papers deal, however, with the simpler type of transflux equilibrium in which all the energy flow traps of the gas at any given point have the same temperature, but in which there is a temperature gradient and a corresponding heat flow by radiation and conduction.

The more complex case of transflux equilibrium in which each energy flow trap carries its own different temperature was barely mentioned in the Symposium. Such cases occur when actual combustion is proceeding, *e.g.*, in the inner cone of a Bunsen flame and in a diffusion flame such as occurs in a metallurgical or boiler furnace. Ribaud regards "temperature" as meaningless under such conditions.

II. Temperature Measurement in Conditions of Thermodynamic Equilibrium

Schulze of the Physikalisch-Technische Reichsanstalt summarized recent work on metallic materials for thermocouples, mainly aimed at obtaining couples which will give repeatable results when subjected to high temperatures and corrosive atmospheres. The work on the noble metals gives the more striking results and two couples are outstanding. Feussner developed one consisting of pure iridium against 60 per cent rhodium and 40 per cent iridium which could be used up to 2000 °C, while Pirani and Wangenheim used a couple composed of pure tungsten against 75 per cent tungsten and 25 per cent molybdenum up to 3000 °C for use in inert gases.

Modern developments in optical and total radiation pyrometers and in millivoltmeters were summarized by Matthews and Bowen. A considerable part of the discussion centered around the question of the relative importance of sensitivity, robustness and high internal resistance in the latter instruments, Schulze suggesting that a value of from 700 to 1000 ohms internal resistance is desirable, while Foster stated that it should be anywhere from 7 to 2000 ohms, according to the duty required.

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* In discharge phenomena at low pressures, temperatures of different orders of magnitude are frequently met with in one and the same place.

III. Simple Transflux Equilibrium

All the remaining papers refer in one way or another to the problem of measuring a gas temperature when there is a flow of heat from or to the surrounding walls, *i.e.*, to the simpler type of transflux equilibrium.

The use of the color pyrometer for measuring the temperature of a luminous gas flame or of objects inserted in a gas stream is proposed by Naeser as a method of overcoming the difficulty caused by the absence of blackbody conditions. Applications of the color pyrometer in the steel industry are described and the instrument is referred to in several of the papers in the applied section.

Other methods of estimating the true gas temperature with simple transflux equilibrium conditions are the suction pyrometer and the use of thermocouples of varying diameter. These devices are dealt with both theoretically and experimentally. Thus, Fishenden and Saunders calculate nomograms from which the radiation error and the error in slowness of response can be read for various thermocouple diameters and gas velocities. Schack and Bosanquet also give methods for calculating the error when using suction pyrometers. Five papers describe different arrangements of such instruments for special purposes. The impression left by these papers is that, although the suction pyrometer is a useful instrument, it cannot be guaranteed to give the true gas temperature without special investigation of the conditions obtaining in each case.

IV. Complex Transflux Equilibrium

Simple transflux equilibrium occurs in industry principally in waste combustion gases where no chemical reaction is proceeding, but where the gas is at a different temperature from the solids present, especially the walls of a chamber or pipe. Where an irreversible chemical reaction is in progress, the situation becomes more complex, and the methods of temperature measurement applicable to simple transflux equilibrium are no longer sufficient. The problems which arise are discussed by Ribaud, who describes the technic used at the Laboratoires des Hautes Températures in Paris, which largely consists in refinements in technic described earlier in the literature. The sodium line reversal method, originally proposed for nonluminous flames, has been developed and applied to a study of flame temperatures in internal combustion engines. A photographic recording system based on the Kurlbaum method of measuring the temperature of luminous flames has also been worked out by Ribaud and his collaborators. It was, however, made clear in Ribaud's paper and in the discussion that these methods are not applicable to those portions of a flame in which the chemical reaction is proceeding, particularly the blue cone of a Bunsen flame, to which Ribaud has given special attention. It must therefore be concluded that at the present time no satisfactory methods of temperature measurement are available for conditions of complex transflux equilibrium. It is even doubtful whether from a theoretical point of view a satisfactory definition of temperature under these conditions can be given at all.

V. Industrial Temperature Measurement Problems

The remaining papers deal with the particular problems facing individual industries. At high pressures, the transfer of heat by convection is improved, but the insertion of the thermometric instrument is a matter of considerable difficulty and the readings of fluid instruments are likely to be upset. Producer gas, owing to its high emissivity, can be accurately measured by a bare fine-wire couple, whereas in boiler furnaces, a suction pyrometer is necessary, although at the airheater a simple thermocouple is sufficient. In glass regenerators, a fine-wire bare couple is in many cases sufficiently accurate. In the chemical industry, the problems are mainly due to corrosion, and the increasing use of pure alumina is mentioned in this connection.

Conclusion

The problem of gas temperature measurement, when there is heat transfer from the gas to the walls, has been fairly thoroughly covered, and close agreement was shown in the views expressed by engineers and scientists from several countries. For this reason, the whole of the papers and the discussion merit close study by anyone who is concerned in the practical aspects of this complicated problem. On the other hand, the Symposium showed that quite apart from the problems connected with methods and errors of measurement, emphasis must be laid on possible misconceptions of the statement of the problem. More particularly, in certain cases, a simple definition of temperature is not possible, so that values given for "temperature" are meaningless. The commonest example of such a case is the flame in which irreversible chemical reaction is taking place, where it would be quite meaningless to determine a temperature and expect to be able to use it with ordinary formulas for radiation and convection heat transfer.

Local Temperature Differences as Occurring in Evaporation, Condensation and Catalytic Reaction

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I. Introduction

In an early state of heat exchange studies, engineers used to assume temperature jumps, wherever heat energy was transferred between solids and fluids, or between liquids and gases. This assumption was based on Newton's equation of heat transfer

$$q = hA(t_1 - t_2) \tag{1}$$

where q is the rate of heat flow between a surface and a fluid in contact with it;
h is a coefficient of heat transfer, defined by the equation;
A is the area of the surface;
t_1 is the temperature of the surface;
t_2 is the temperature of the fluid.

This equation indeed seems to state a discontinuous temperature drop $t_1 - t_2$. Only in this century it has been interpreted in a different way, and now one knows that discontinuities of temperature occur almost exclusively in the cases of radiation and of gas convection at low pressure, though a steep slope in temperature often may take place. Sometimes, however, no reason at all seems to exist for a temperature difference, for instance at the interfacial surface of a two-phase system, where evaporation and condensation occur. Actually this holds for thermodynamic equilibrium conditions only, and physical theories generally assume that the same mass evaporates and condenses in any time interval. Differences in these masses, if any, are said to be due to the diffusion of the vapor on the surface or to mechanical leading away of vapor or liquid. But the effect of such deviations from equilibrium conditions is just what is interesting in many engineering processes, and it causes temperature differences where none are expected.

In the present paper a few practical cases (evaporation, condensation, catalytic reaction) will be treated where dynamic conditions produce local temperature differences. The best known of these processes, evaporation, will be dealt with more in detail than the others.

II. The Temperature Excess of a Boiling Liquid Over the Produced Vapor

In this section, following Drew and Mueller,[3] we shall distinguish between "ordinary boiling" (what they call "nucleate boiling") and "film boiling." Ordinary boiling issues from small cells, which, *e.g.*, can be tiny gas bubbles or curved cavities of a surface; the second is a particular mode of evaporating, in which large bubbles originate from a vapor film on the heating surface. Besides boiling we shall deal briefly with the process of evaporating without formation of bubbles.

(1) Ordinary Boiling in Low Liquid Columns. Already in 1909, a small temperature excess of boiling water over the leaving steam had been noticed by Henning[8] in his measurements of the latent heat between 100 and 180 °C. When in 1928 the present author[10] had observed the same effect at 180 °C and 210 °C, he began to study further whether that result was due to errors of observation or to actual physical reasons. This was done in two series of investigations, one connected with measurements of the latent heat of the water, the other devoted to the process of evaporation.

In the experiments on the latent heat, first of all by continued improvement of the arrangement and the technic of measurement, all conceivable sources of error were excluded, for instance, impurities of the water, the formation of drops on the walls, the influence of hydraulic pressure, and conductive heat losses.[19,20] Thus in the last-mentioned paper it could be stated that the temperature of boiling water actually was higher than that of the steam. Further it was found by exact pressure measurements that the steam temperature was identical with the equilibrium temperature of saturation, so that the water must have been superheated. To our disappointment we could not state any such effect in the next step of our investigation;[22] but finally [23] we found out that the decrease of the observed effect almost from each investigation to the next one was due to the fact that each subsequent investigation had been performed at a higher saturation pressure and temperature than the preceding one, and that the effect sought decreased with increasing pressure. This can be seen from Fig. 1, which has been derived from about 34 measurements in different arrangements at pressures between 14.7 and 2873 lbs per sq inch, corresponding to saturation temperatures of 100 to 365 °C.

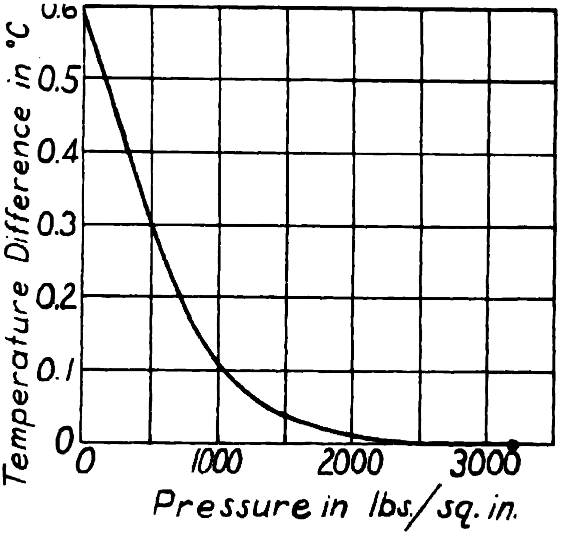

Fig. 1.

Temperature difference between boiling water and steam.

The temperature difference tends to zero if one approaches the critical point (3200 lbs per sq in, 374.1 °C) where the surface and all differences between water and steam disappear.

As to our studies of the process of evaporation, we had to consider the theoretical equation of W. Thomson (Lord Kelvin):

$$p_v = p_l + \frac{2\sigma}{R} \qquad (2)$$

where p_v = the vapor pressure on the inside of a spheric vapor bubble in a liquid at equilibrium conditions;
p_l = the liquid pressure on the outside of the vapor bubble;
σ = the surface tension of the liquid against the vapor;
R = the radius of the bubble.

From this it follows that between a vapor bubble at the pressure p_v and the liquid surrounding it, equilibrium can exist only if their common temperature, t, is higher than the saturation temperature, t_s, would be, if in their place a plane surface at the hydraulic pressure p_l existed. A vapor bubble and its close environs at the temperature t, as represented in Fig. 2, in a liquid at the temperature t_s would be cooled by heat conduction to the bulk of the liquid; thus the vapor in the bubble would begin to condense and the bubble would collapse.

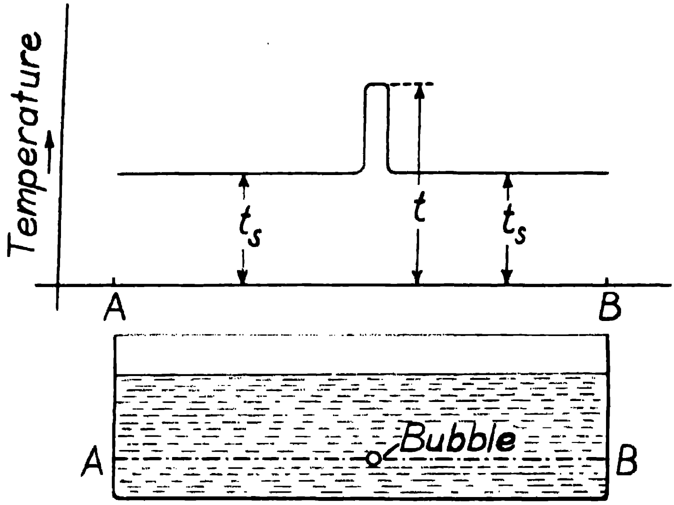

FIG. 2. Temperature distribution incompatible with stability of a vapor bubble.

Thus a bubble in equilibrium can last only if no heat is conducted away, that is, if the liquid around it is superheated too, which, on the other hand, means nonequilibrium for the bulk of the liquid.

The technical process of evaporation or production of a vapor is a nonequilibrium process. According to the Equation (2), it would be impossible for a bubble to originate at $R = 0$, and boiling will not start unless finite curvatures are present, such as formed by wall roughnesses, or by nuclei like gas bubbles or other impurities in the liquid. Then tiny vapor bubbles originate at a temperature of the liquid exceeding the saturation temperature, which corresponds to the pressure inside the bubbles, whereas the vapor produced is at this saturation temperature. The temperature between liquid and vapor tends to equalize; but because of the quick rising of the bubbles, this will not be completed. Therefore, the superheating of the liquid may last, even when the radius of the bubble has increased so much that $p_v - p_l$ becomes negligibly small.

Indeed all our experiments showed that the bulk of the liquid was at a higher temperature than saturation, so that a steep drop (although probably not a real discontinuity) occurred on the level between the liquid and the vapor.[18, 21]

Fig. 3 shows two characteristic examples of this behavior, found with boiling water. According to these graphs, beginning with the temperature of the heating surface, the water temperature decreases greatly in the close proximity of that surface. This indicates that a thin layer exists, which is not mixed by convection. The temperature drop in this layer (not to be completely seen in the figure) depends on the heat flow per unit time and unit area, which we shall call "specific heat flow" and denote by *H*. This amounted to 90 B.t.u. $ft^{-2}hr^{-1}$ in the upper part of the graph, and 13,600 in the lower one; both referred to a polished heating surface, and the temperature drops were 0.4 and 10.1 °C respectively.

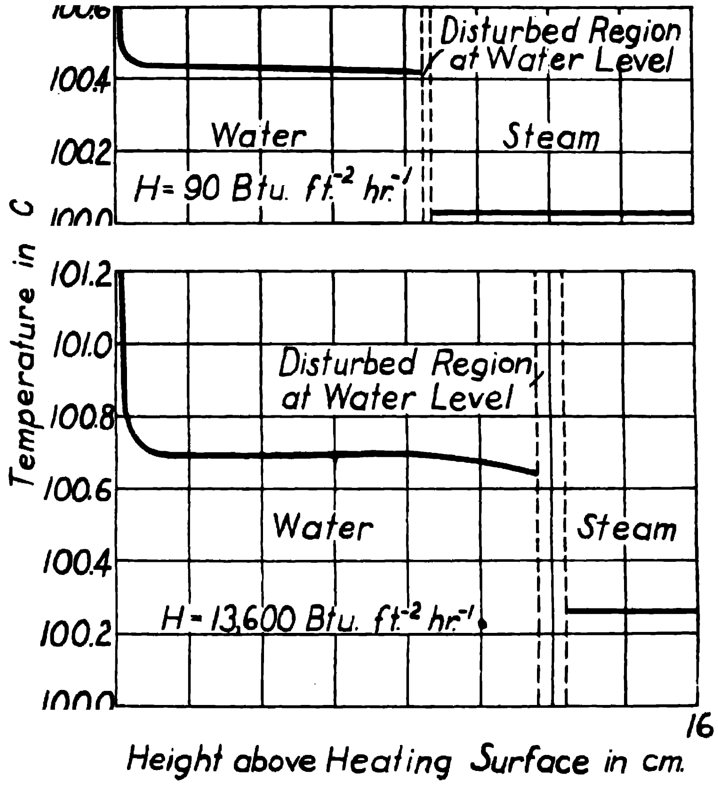

FIG. 3. Temperature distribution in ordinary boiling.

Proceeding in the direction toward the water level, we observed a negligible decrease of temperature in the bulk of the water, whereas owing to the change of hydraulic pressure a decrease of 0.2 and 0.3 °C, respectively, would have been expected. From this we concluded[21] that, even with a heating of only 90 B.t.u. ft^{-2} hr^{-1} the convective mixture was sufficient to overshadow the effect of the hydraulic pressure. A more thorough explanation will be given later.

The most interesting result, however, was how little the specific heat flow, *H*, influenced the temperature difference between water and steam. Whereas *H* was increased 150 times, the temperature drop at the liquid level remained almost unchanged at 0.4 °C, and also in other experiments the temperature drop did not change much with H. This is very strange, because one might expect that the temperature difference would increase about proportionately with the heat flow. It is possible, however, that in a thin layer of water below the surface, a steady temperature slope exists which increases with the heat flow. Owing to the inquietude of the water level in boiling, we could not decide this question.

(2) Evaporation Without Bubbles. But Heidrich[7] found such a slope in evaporating highly pure and gas-free water from an interfacial surface of 54.5 cm^2 without formation of any bubbles at all. In a thin layer (0.05 or 0.1 cm) at the water level a fairly linear temperature change was found, and at a greater depth (1 cm and more) the temperature was almost constant, in agreement with our results. The slope of the water temperature in the thin layer mentioned was stated to increase with the specific heat flow, less than proportionally, however. Heidrich tried to calculate the thickness of the layer from the temperature drop, which he had measured in the axis of his vessel, on the assumption that it was due to heat conduction in a vertical direction only. This led to a thickness much smaller than that observed; so Heidrich assumed that by convection the boundary layer was thinned out, between the center and the edge of the water surface. The present author[12] showed that, as an average, the layer would have been two or three times smaller than was calculated from the temperature drop in the center. Without using Heidrich's assumption of mere conduction in a boundary layer, he demonstrated that, owing to a peculiar kinematic similarity of convection in both cases, the temperature drop between the water and its free surface in Heidrich's experiments must have been equal to that between the heating surface and the water in his own experiments. This has been checked in a range up to $H = 5900$ B.t.u. ft^{-2} hr^{-1}, and found to be in reasonable agreement. By this it has been shown why, in evaporating without boiling, the temperature difference between the bulk of the liquid and the vapor depends on the heat flow.

(3) The Mechanism Controlling the Temperature Excess in Ordinary Boiling. In the case of boiling, on the other hand, an almost invariable temperature difference seems to be held automatically.

The mechanism which effects this seems to be controlled by the number of places from which columns of steam bubbles rise. We showed[21] that steam bubbles originate only on a few points of the heating surface, and in another paper[24] that the number of these places is roughly proportional to the specific heat flow. For a polished horizontal heating surface of 78.5 cm^2, and in the range up to about 18,400 B.t.u. ft^{-2} hr^{-1}, I concluded from these experiments that for every increase of the specific heat flow by 700 B.t.u. ft^{-2} hr^{-1} one more steam column was formed. From this, one easily can calculate that each column of steam bubbles in our experiments received about 59 B.t.u./hr, and with a latent heat of 970 B.t.u./lb, that 0.061 lb of steam was formed per hour in each column. Because one has to consider the columns of steam bubbles as generating the superheating effect, it follows that by an increase of the heating energy, only the number of steam columns is increased, and therefore the distance of action of each column is reduced; but the temperature difference between the water and the vapor in each column remains almost invariable.

There are secondary effects, however, owing to differences in the roughness of the heating surface and to the height of the liquid above it. We shall consider here only the latter influence.

(4) Ordinary Boiling in Rather High Liquid Columns. The effect of the change of hydrodynamic pressure and therefore of the boiling temperature upon the temperature difference has been studied by two of my former co-workers, Fritz and Homann,[6] in an arrangement developed by me for this purpose. The method consists in varying the depth of the boiling liquid in a vessel which is heated by a horizontal heater on the bottom and perfectly insulated against heat losses. The equipment allowed experiments with water, 20 to 90 cm deep, in a cylindrical vessel 15 cm wide, in which tubes 5 cm or 10 cm wide, open on both ends, could be placed concentrically in order to study the influence of width.

This investigation, first of all, confirmed the fact that the specific heat flow, H, which was varied from 1840 to 25,800 B.t.u. ft^{-2} hr^{-1}, does not influence the temperature distribution at all. But some other results were rather unexpected.

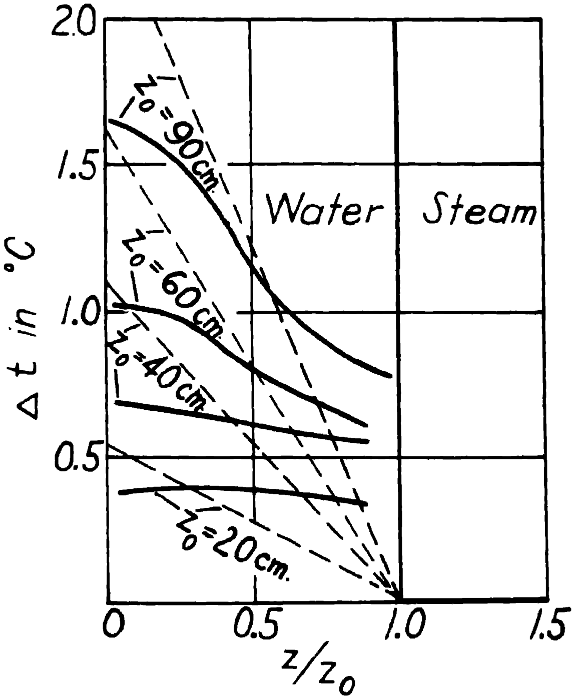

FIG. 4.

Temperature distribution in ordinary boiling ($z_0 = 20$ to 90 cm).

——— Experimental curves.

— — — Saturation line for hydrostatic pressure.

Fig. 4 shows temperature differences, Δt, between the water and the steam above the surface, at different heights, z, over the heating surface for four water depths z_0. The curves in the graph are averages of all experiments of the authors, including those with concentric tubes, as described. No measurements were made at distances less than 1 cm from the heating surface. The temperature excess of the latter was 2 to 11 °C, according to the heat flow, and one must imagine that the temperature excess Δt, of the water in contact with the heater increased up to the same values. The oblique straight lines in the graph show the temperature differences for equilibrium conditions due to the hydraulic pressure.

One recognizes that the temperature of the water does not follow these lines at all, but that a very odd temperature distribution exists. Close to the heating surface the water is much superheated (not represented in the figure), on an average by $\Delta t = \frac{2 + 11}{2} = 6.5$ °C. Proceeding to larger values of z/z_0, Δt decreases and becomes smaller than the temperature difference in equilibrium; but later the

Δt-curve crosses the equilibrium line for a second time, so that close to the water level the water is superheated in any case, namely about 0.3 °C for the water depth $z_0 = 20$ cm, and 0.75 °C if $z_0 = 90$ cm.

This strange temperature distribution apparently is caused by the convection which drives superheated water from the heating surface up to the level; although it is cooled in this way, it arrives at still higher than equilibrium temperature which is less at the level than at the heating surface. The cooler upper water, on the other hand, is moved toward the heating surface; although it is heated in this way, it arrives at still lower than equilibrium temperature which here is more than close to the level. The fact that the circulating water carries steam bubbles, more of them of course upward than downward, complicates the process even more. For small depths (for instance $z_0 = 20$ cm) the mixture is almost complete (lower curve in Fig. 4). For this reason we did not find the influence of depth in our former experiments[21] which were restricted to $z_0 \gtreqless 15$ cm. Damping the convection by bringing the tubes mentioned (10 and 5 cm wide) into the boiling vessel, the curves of Δt came closer to the equilibrium line.

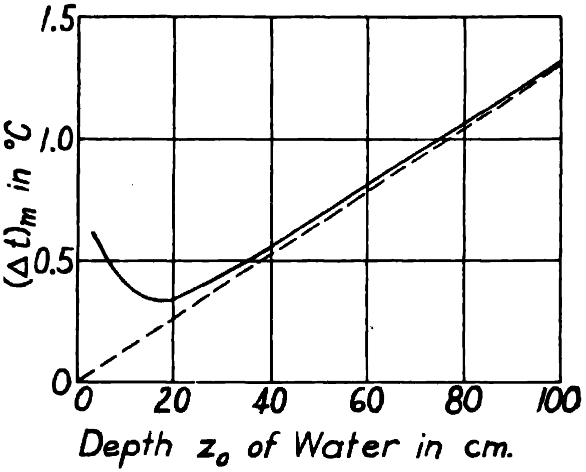

FIG. 5.

Mean temperature excess in ordinary boiling.

Even more surprising is another representation of the results to which the authors came by integrating the temperature excess, Δt, over the whole depth of the liquid (Fig. 5). According to this graph, only for water depths $z_0 < 20$ cm, appreciable differences exist between the mean observed and the mean equilibrium temperature, but practically none for $z_0 > 20$ cm. I would interpret this result as a proof that the fluid is mixed so well by convection that a sort of heat balance exists at a given time, that is, if all heat supply and motion were stopped at once, the internal energy of the whole mass of water would be almost the same as though each part of it were in equilibrium; therefore, no more heat exchange between the water and the steam would have to take place as an average, with the exception of a layer of warm liquid above the heating surface which would not have been mixed as yet. The authors mention that this is the very source of superheating. Its influence, of course, decreases with increasing water depth, so that the two lines in Fig. 5 approach each other with increasing z_0.

The value of this representation should not be overestimated, however. It shows only what would occur under the artificial assumption of suddenly stopping the whole process, but does not contribute much to an explanation of what really happens if the process runs. The weak point of the representation is the plain integration of the temperature differences over the depth, whereas an integration considering the dynamic effects would give an entirely different picture. According to our high-speed camera measurements on steam bubbles,[5,11,13] the coefficient of heat transfer, h, on the surface of a bubble is very large, as long as the bubble adheres to the heating surface; nevertheless its contribution to evaporation in this period amounted only from 2 to 40 per cent of the total energy of evaporation, owing to the small size of the bubbles as long as they adhered to the heater. For rising bubbles, on the other hand, we found h to be almost constant, and therefore the heat transfer increased while the bubbles grew. Thus, particularly for those bubbles which break off the heating surface when still very small, in the region near the level where the liquid is superheated and the bubbles become large, the greatest part of the heat energy is transferred. For this reason, although the ordinary average of the temperature excess may be very small, by the concurrence of the distribution of the water temperature and of the size of the steam bubbles over the water space, the local temperature excess of the water remains decisive for the evaporation in boiling.

This temperature excess really is the clue to an understanding of the boiling process. Before it was recognized that the heat energy makes a detour from the heating surface through the liquid to the bubbles, one had to assume that all the vapor was formed on the heating surface and by that part of evaporation into the rising bubbles, which is due to the decrease of the hydraulic pressure. But these kinds of evaporation were much too ineffective to explain numerically the actual rate of evaporation in boiling. Bošnjaković[1] was the first to take in account the heat conduction from the warmer liquid into the cooler vapor bubble; and our high-speed camera experiments yielded more quantitative results showing that the large effect of the small temperature difference between liquid and bubbles is due to the large total area of the surfaces and the high coefficient of heat transfer involved.

(5) The Question of Temperature Discontinuities. Unfortunately, none of these investigations definitely decides the question whether, on the interfacial surface between liquid and vapor, a real temperature discontinuity occurs in evaporation. In our experiments a disturbed region existed on the level (see Fig. 3), which made this decision impossible. Heidrich, on the other hand, by extrapolating to the water level his curves of the water temperature in the axis of his vessel, obtained definite values for the temperature excess of the water. From these one would calculate a jump of about 1.8 °C per 10,000 B.t.u. ft^{-2} hr^{-1}, without considering, however, that it may be different away from the center; but Heidrich himself was afraid that this temperature excess might not be real, but might be caused by heat conduction in his thermocouple.

Also, in our analysis of the heat transmission between water and a steam bubble, we did not assume a discontinuity at the surface of the bubble except at the very origin of the bubble, which I have called an "explosion in microscopic scale."[11,13] In this moment the surface temperature must be considered as dropping discontinuously from the water temperature to the lower temperature value of saturation.

With this exception, no evidence exists that any particular temperature jump or drop occurs in evaporating a liquid (whether it boils or not), besides the temperature differences due to heat conduction and convection.

(6) Film Boiling. This holds also for the case of film boiling as dealt with by Drew and Mueller,[8] Sauer, Cooper, Akin and McAdams,[27] and others. "Film boiling" occurs if the temperature of the heating surface is so much over saturation temperature that the surface instantaneously is covered by a vapor film which sets up a large heat resistance, so that the heat transfer between the heater and the bulk of the liquid becomes very small, and the evaporation of the latter actually occurs at the interface between the vapor film and the liquid, in close analogy to film condensation. If one approaches "film boiling" by increasing the specific heat flow, the transition from ordinary to film boiling will be accompanied by overcrowding of the bubbles adhering to the heating surface.[13] These then will coalesce into a thin film, in which the vapor will become superheated. The temperature of that vapor will sharply decrease from the solid heater surface to the interfacial surface between the film and the bulk of the liquid. Also, there the vapor will be superheated and the lowest liquid layer as well, for this surface of the vapor film corresponds to the metallic heating surface in ordinary boiling. Besides this, radiation from the heater surface will contribute to the heating. The large vapor bubbles originating in the film probably will contain superheated vapor also.

The paper of Drew and Mueller, besides their own experiments, contains an excellent historical survey of this kind of boiling, which from a practical standpoint might better be called a hindrance of boiling. It must be avoided in ordinary practice, and the investigations about it just show the conditions under which it would occur, and which therefore must be avoided.

III. Temperature Drop Between a Condensing Vapor and its Condensate

From a theoretical viewpoint condensation on a plane, liquid surface simply should be the reverse of evaporation, and drop formation a sort of inversion of the formation of steam bubbles. W. Thomson's equilibrium equation (2), for instance, holds for drops as well as for vapor bubbles; one has only to replace the bubble radius, R, by the negative value of the drop radius R.

So one certainly can predict much about the temperature differences to be expected; but there are some important practical differences. In large-scale production of vapors, for instance, the evaporation from the liquid level plays a secondary role only, and generally rather high liquid columns are to be considered. In condensation, on the other hand, extremely thin liquid layers occur, and condensation on those, called film condensation, prevails in industrial applications. The most important kind of evaporation is boiling, and one has to consider the fact that vapor bubbles originate at the heating surface and wander through the liquid, whereby they grow by the influence of the small temperature difference between their surface and the liquid. In condensation, however, the formation of drops has been a rather exceptional case until now. It must be treated in entirely different ways, according to whether the cooling surface is concerned with it or not; the first case occurs in condensing devices, the other in nozzles of steam turbines.

(1) Undercooling of Steam in Nozzles. Again, besides W. Thomson's equilibrium conditions, the laws of heat conduction and convection are decisive for the temperature differences which occur. As early as 1906 the author, in coöperation with O. Knoblauch,[25] described experiments in which drops pertinaciously remained in highly superheated steam.

On the other hand, it is well known that undercooling of a vapor can occur as well. In certain nozzles of steam turbines, owing to the lack of nuclei of more than molecular size, and to the extremely short time available, condensation of steam is delayed, and only rather far below the saturation temperature are extremely small droplets suddenly formed. We shall not deal in detail with this case, which has been studied very thoroughly by G. T. Wilson, Stodola, Martin, Yellott,[28,29] and others. It may be mentioned only that undercooling of steam by as much as 20 °C has been observed, and that below the saturation line of the steam charts, in a region where steam in equilibrium contains 4 to 5 per cent moisture, there is a limit, called the "Wilson line," which indicates the maximum possible temperature lack. The droplets with a radius of approximately 62 (10^{-9}) cm which are formed under ideal conditions, must originate in an explosive manner as vapor bubbles do; and at the moment of originating, there may exist on the surface a considerable discontinuity between the saturation temperature of the droplet and the lower temperature of the undercooled vapor around it, which corresponds to the discontinuity occurring when a vapor bubble originates.

(2) **Film Condensation.** As to temperature differences in devices for condensation, we shall first consider film condensation and then dropwise condensation. Whereas in evaporation on a plane surface we could not definitely decide whether the temperature drops at the liquid level or not, in the case of condensation it seems to be certain that a temperature drop, although very small, takes place. In Nusselt's liquid film theory, one of the assumptions is that the surface of the film in contact with the vapor is at saturation temperature. It is shown in that theory how the condensation depends on the thickness of the film. But this involves the condition that the temperature of the interfacial surface must be lower than the vapor temperature. For, as I expressed it in a previous paper [11] "if the condensing steam is in contact only with a surface of liquid, and this is always at the saturation temperature, it is hard to comprehend how this vapor can know the thickness of the liquid layer on which the rate of condensation is said to depend. In other words, if the temperature of the film on the steam side is always exactly equal to saturation temperature, the same mass will be condensed, notwithstanding the thickness of the film." From this I demonstrated that the temperature of the liquid surface on the vapor side of the film must be slightly below saturation temperature. Incidentally, I had envisaged, but not proved this long before.[9] A direct experimental proof would be very difficult, because the liquid layer in which the temperature drop occurs is extremely thin. As to the condensation of superheated vapors, F. Roecke performed measurements on steam flowing in a vertical direction through an annular space 2.4 cm wide, which was formed by two coaxial vertical tubes. The inner tube was held at 107.3 °C, the outer one being well insulated. The steam entered the upper end of the device at 20.5 lb/sq inch and 159.4 °C at a mean velocity of 36 ft/sec. At 55 cm and 105 cm below the entrance section, constancy of temperature (135 °C) was observed in a range from 1 to 0.1 cm distance from the cooled wall. In the last 0.1 cm from the wall the temperature dropped from 135 °C to saturation temperature (109.6 °C). The present author [11,18] has explained this in the following way: Particles of steam coming from the zone distant 0.1 to 1.0 cm do not return from the cooling surface, but are held there by condensation; a zone close to the wall and 0.1 cm thick is a transition layer that contains a mixture of superheated and saturated steam. When we [13,18] studied the temperature distribution in a tube 4 cm wide in which steam of atmospheric pressure entered at 325 °C and was condensed on the wall, we observed a temperature drop between about 290 and 100 °C in the last 0.1 cm from the wall.

Bošnjaković [2] has developed an interesting theory of film condensation. He pursued the exchange of molecules which takes place at the surface, and considered the small temperature excess in evaporating. One of the results of this theory is that superheated steam does not begin to condense unless the cooling surface is considerably below saturation temperature, according to the equation

$$\frac{p_l}{\sqrt{T_l}} = \frac{p}{\sqrt{T}} \tag{3}$$

where p and T are pressure and absolute temperature, respectively, of the superheated steam and p_l and T_l are the corresponding values for the saturated liquid.

The temperature of the wall must be less than T_l if condensation is to take place at all. For instance, with steam at 1.033 kg/cm^2 (14.7 lb/sq inch) and 325 °C (T = 598 °K), $p_l/\sqrt{T_l} = 423$ kg cm^{-2} (°K)$^{-\frac{1}{2}}$, and one point of the saturation curve only corresponds to this relation, namely $T_l = 366.4$ °K ($t_1 = 93.3$ °C), $p_l = 0.81$ kg/cm^2. Thus, 100 °C being the saturation temperature at $p = 1.033$ kg/cm^2, the superheated steam under consideration would begin to condense only if the surface were about 7 °C below saturation temperature.

Bošnjaković explains this as follows: For condensation a certain density of the steam molecules is necessary. With saturated steam this density exists, so that condensation can take place if the cooling surface is undercooled slightly. With higher temperature at the same pressure, the density is smaller, so that the surface must be brought to a temperature considerably lower than that of saturation. This would explain certain discrepancies in condensation tests, which for instance led Nusselt [23] to the conclusion that there must exist cases in which superheated steam in contact with a metal wall below saturation temperature does not form a water film, but becomes undercooled.

Bošnjaković has checked his theory by experimental results, which had been found by the present author with some co-workers,[16] and particularly, in agreement with an anomaly discovered by us,[17] he stated that sometimes the temperature in the case of flowing superheated steam becomes higher if condensation on the cooling surface is increased. The velocity and temperature distribution across the flowing steam, however, are not considered in that theory, and more work seems necessary to confirm and improve it.

(3) Drop Condensation on Solid Surfaces. Concerning dropwise condensation on surfaces where relatively large nuclei are always present, Eucken [4a] and Emmons [4] independently have developed theories of almost the same kind. In addition to other results, it is shown that a blanket of undercooled vapor is formed on the cooling surface between the drops. Where this vapor comes into contact with a drop, condensation will proceed very rapidly. There will thus be produced a local reduction of pressure which in turn will set up violent local eddy currents in the vapor between the drops. This mechanism is said to be responsible for the very high heat transfer coefficient in drop condensation. The present author has envisaged similar ideas [11] in the following sentences: "It must be assumed that the steam particles in the closest proximity of the cooling surface hit it at considerable speed, because by the condensation of the preceding steam particles space becomes suddenly free. Thus the steam condenses in tiny droplets, which *in statu nascendi* transfer their heat of condensation to the cooling surface. Thereby undercooling of the steam may possibly take place."

According to Emmons' theory, the undercooled steam would be in contact with the cooling surface. This then could be free of liquid only to the Wilson line. Should the surface be still colder, liquid would be formed. This, as explained elsewhere,[18] could originate in the form of unstable shreds of a liquid layer, which then would be peeled off and rolled together to droplets, giving space for the repetition of this process. It would be connected with an intermittent warming up of the surface above the Wilson temperature by the heat of condensation.

IV. Temperature Difference between Reacting and Flowing Gas on Catalysts

As a third example of temperature differences occuring in places where the phase or composition of a fluid changes, the author recently studied the case of a catalytic reaction.[14, 15] Here the temperature difference is due to the following facts: A catalytic reaction is supposed to take place immediately on the surface of the catalyst which itself does not take part in the process. Considering, for instance, the exothermic reaction of a gas mixture, with the participants of the reaction in a steady flow, the heat produced on the surface cannot enter the catalyst, but will be given up to the fluid. For this reason the catalyst surface acts like the surface of a heater, and according to the rules of heat transfer a difference must exist between the temperature of the gas reacting on the surface and the temperature of the bulk of the flowing gas. In order to measure this, a catalytic chamber of simple geometric shape was used, namely an annular space, 0.2 cm wide, between two long, coaxial nickel tubes. The inside of the outer tube was covered with nickel black as a catalyst. A shiftable thermocouple was arranged inside the inner tube, and a dozen thermocouples were fixed on the outside of the outer tube. Using a process with an exactly known heat of reaction (hydrogenation of ethylene into ethane), the heat produced could be determined from the mass of the flowing gas and its temperature increase. The temperature drop on the catalytic surface was reduced by a mass transportation between the surface of the catalyst and the bulk of the flowing gas mixture. This was caused by the difference of concentration of ethane in the mixture, this concentration being larger on the catalyst than on the surface free of catalyst. By varying the radial intake or output of heat energy by means of electrical heating coils arranged on an outer coaxial tube, the effect of the mass transportation could be eliminated. Eventually, temperature differences between the catalyst and the main mass of gas were found which, for conversions of 0.55 to 1.28 per cent of the ethylene into ethane, amounted 0.7 to 1.6 °C, or roughly 1 °C for about 1 per cent conversion. This holds for streamline flow of the gas mixture. The effect would be larger for a higher output than 1 per cent with the same catalytic surface, but smaller for turbulence and tubes closely packed with catalytic particles. In any case, the average temperature measured by means of any thermometers put into a catalytic tube cannot be considered as identical with the temperature of catalytic reaction; and there are cases conceivable, particularly with spacious catalytic pebbles, where the difference may be rather considerable.

V. Summary and Conclusions

In processes connected with changes of phase or composition, temperature differences on the interfacial surfaces occur which are due to the non-equilibrium conditions of flow and heat transfer. Though small, these temperature differences may be essential for the process.

This is particularly shown for the process of evaporation. In the ordinary mode of boiling water, for instance, a difference of less than 1 °C between the bulk of the liquid and the steam bubbles is sufficient for transmitting the main part of the energy of evaporation. This energy makes a detour from the heating surface through the liquid to the bubbles, the direct heat transfer between the metallic surface and the steam being much too weak, even if rather large temperature differences would be admitted as observed in the so-called "film boiling." It is demonstrated that in ordinary boiling, it is not the average of the temperature differences between water and steam taken over the water column that is decisive, but the peculiar distribution of the temperature excess of the water, together with the growth of the rising bubbles. The observation that the rate of heating does not influence this temperature excess is explained from the very mechanism of boiling.

In film condensation, slight undercooling of the liquid below saturation temperature seems to be necessary in any case. In the case of superheated steam, however, a rather considerable undercooling of the liquid is claimed by one of the existing theories. Undercooling of the steam is usual, and is well known in turbine nozzles. A recent theory on drop condensation at surfaces likewise states that the vapor must be undercooled.

Neither in evaporation nor in condensation have discontinuities of temperature been stated by direct observation; but it has been shown that jumps may occur in the very first moment when a vapor bubble or a drop originates.

As a third example is given the apparent temperature difference which takes place at the surface of catalysts in the reaction of a gas mixture. Here the surface temperature is identical with the temperature of reaction, and according to the laws of heat transfer the temperature of the gas flowing close to the surface must be lower than this for an exothermic, and higher for an endothermic reaction. The author recently has confirmed this by experiments, in which ethylene was converted into ethane by hydrogenation.

Generally one must keep in mind that in mechanical and chemical engineering the transformation of substances into another phase or composition does not take place in equilibrium, but under dynamic conditions. Therefore, one cannot use always the equilibrium temperature, common to the participants of the process, but must expect and consider temperature differences on the interfacial surfaces, which often form the very clue to an understanding of the mechanism of the process under consideration.

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Temperature Measurements in Air Conditioning

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Temperature measurements are of fundamental importance in air conditioning. They are generally used for determining the overall performance of an air conditioner, which depends on the product of the air flow and the change in heat content of the air passing through it. Also, they are necessary for investigating the performance of a furnace, which is used as the source of heating, and of a refrigerating system, which is used as the source of cooling. Engineers have learned that the capacity of an air conditioner cannot be determined by merely passing an anemometer over the discharge area to measure air velocity and placing a thermometer in the air stream to measure its temperature. They have learned that many precautions are necessary in the measurement of both air velocity and air temperature.

The purpose of this paper is to discuss some of the problems involved in obtaining accurate air-conditioning temperature measurements, and to describe methods used in a development laboratory of a large manufacturer.

One of the greatest sources of difficulty in air conditioning testing is the nonuniform distribution of air velocity and temperature over the discharge area or across an air stream elsewhere in the test set-up where it is necessary to measure temperature. A person might at first expect that the correct average temperature could be obtained by dividing the cross-sectional area of the air stream into a number of equal areas and taking the arithmetic average of the temperatures of each of these smaller areas. However, further consideration will reveal that this is not necessarily true, and that the velocity must be considered together with the temperature at each point where it is measured. The true heating or cooling capacity of the unit is the summation of the capacities for each of the small areas used in the survey, and the true weighted average temperature is that value which is determined by figuring backward, using this capacity and the total air flow. An example will illustrate:

$v = 0$ $t = 120$	$v = 0$ $t = 123$	$v = 0$ $t = 124$	$v = 0$ $t = 125$	$v = 0$ $t = 124$
$v = 175$ $t = 123$	$v = 55$ $t = 124$	$v = 102$ $t = 126$	$v = 70$ $t = 128$	$v = 205$ $t = 127$
$v = 182$ $t = 126$	$v = 170$ $t = 128$	$v = 165$ $t = 130$	$v = 180$ $t = 132$	$v = 195$ $t = 131$
$v = 210$ $t = 127$	$v = 180$ $t = 128$	$v = 140$ $t = 130$	$v = 170$ $t = 133$	$v = 215$ $t = 132$

Fig. 1. Temperature and Velocity Survey over Discharge Area of winter air conditioner.

A winter conditioner was tested for heating capacity with thermometers located at several places in the discharge air stream in an attempt to obtain the average air temperature. A wide discrepancy was found to exist between the heat given up by the steam in the heating coil and the apparent heat absorbed by the air, plus the calculated jacket losses. Surveys were then made of both temperature and velocity, using an aspirating thermocouple for the temperature measurements to avoid radiation effects. The results, which are shown in Fig. 1, varied greatly.

Table 1 gives a summary of capacity calculations made from these results in three different ways, the first in the most extreme way where the minimum temperature was used for the outlet or discharge air temperature, the second where the arithmetic average was used, and the third where the outlet temperature was correctly obtained by weighting the temperatures and velocities together for all the survey areas. To improve the accuracy, the velocity readings were used as relative values only, and were adjusted so that they gave the same total air flow as the overall air flow measurement for the conditioner. The errors of 15.1, 2.6, and 0 per cent, respectively, for the three methods, confirm the previous discussion in an interesting way.

Table 1. Capacity Calculations for Results of Fig. 1.

	Based on minimum temp.	Based on arithmetic avg. temp.	Based on weighted avg. temp.
Outlet air temperature (°F)	120.0	127.0	128.6
Inlet air temperature (°F)	71.7	71.7	71.7
Heat given up by steam (Btu/hr)	76,000	76,000	76,000
Heat absorbed by air plus calculated jacket loss (Btu/hr)	64,500	74,000	76,000
Error in heat balance (%)	15.1	2.6	0

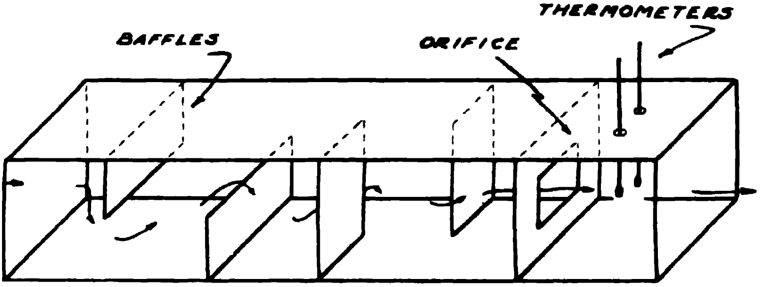

FIG. 2. Simple air mixing box.

Although the temperature and velocity survey method described above gives valuable information and leads to correct results, yet when a person is interested in the true average air temperature only, it is much more practical to obtain this by mixing the air thoroughly before the temperature is taken. Both the American Society of Heating and Ventilating Engineers and the American Society of Refrigerating Engineers have specified the mixing method in their codes.[1,2] However, as Tuve and Seigel have pointed out,[3] it is very difficult to obtain a thorough job of mixing.

A simple type of mixing box or duct is shown in Fig. 2. Note that the baffles are arranged to turn the air twice around a horizontal axis and then twice around a vertical axis. After this, the air passes through an orifice where its velocity is stepped up to give a satisfactory value for taking the wet- and dry-bulb temperature readings.

A more elaborate type of mixing box is shown in Fig. 3. The purpose of the plenum chamber at the inlet is to provide a region of low air velocity where the static pressure against which the conditioner is discharging may be measured. The orifice in this case is made from a steel plate and is used for measuring air flow as well as for providing a place to take the temperatures. The fan is used for overcoming the resistance of the mixing box and for adjusting the air flow or conditioner discharge pressure to the desired value. Since a mixing box is rather large, its walls should be insulated to reduce heat leakage, and the amount of this leakage should be calculated and used in correcting the capacity and temperature results.

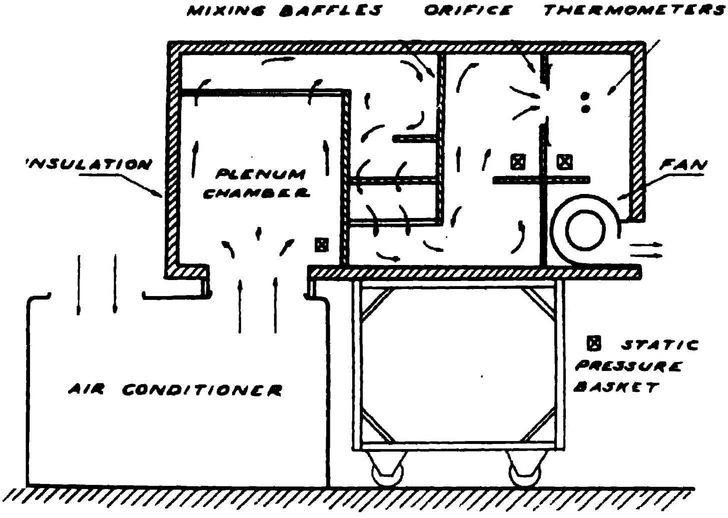

FIG. 3. Special air mixing box equipped to measure air flow and inlet static pressure.

It should be pointed out that a fan is not necessarily a good mixing device. The non-uniform temperature results shown in Fig. 1 were taken at the outlet of a fan.

Another problem closely associated with that of air mixing is the technic of wet-bulb temperature measurement. This is particularly important in connection with the testing of room coolers, because the usual procedure in calculating the capacity is to base the total heat content of the entering and leaving air on wet-bulb temperatures,[2] the difference of which is often very small. It should be pointed out that the thermodynamic properties of air and water-vapor mixtures are such that the wet-bulb temperature alone determines the total heat of the mixture with sufficient accuracy for engineering purposes.[4,5,6] Fig. 4 is a picture of a test set-up where a self-contained air-cooled room cooler is being tested by the A. S. R. E. test code method.[2] The unit under test is enclosed in an insulated box or calorimeter through which the evaporator and condenser air mixing ducts extend.

The method of obtaining wet-bulb temperature measurements is that of dipping a wick-covered mercury-in-glass thermometer bulb into water, placing this in the air stream, and observing the minimum temperature that it reaches. This general procedure has frequently been described by others.[4,7] The wicks, which are the standard cloth type obtained from thermometer manufacturers, are cut to extend about an inch above the mercury bulb. Distilled water is used to prevent liming of the wicks; and as a further precaution the wicks are changed frequently to keep them clean. The thermometer is wetted before each reading; and after it has been replaced in the air stream, the mercury column is carefully watched to be sure that the minimum value is observed. In establishing the procedure for a particular test it is well to wet the bulb a second time and take a check reading.

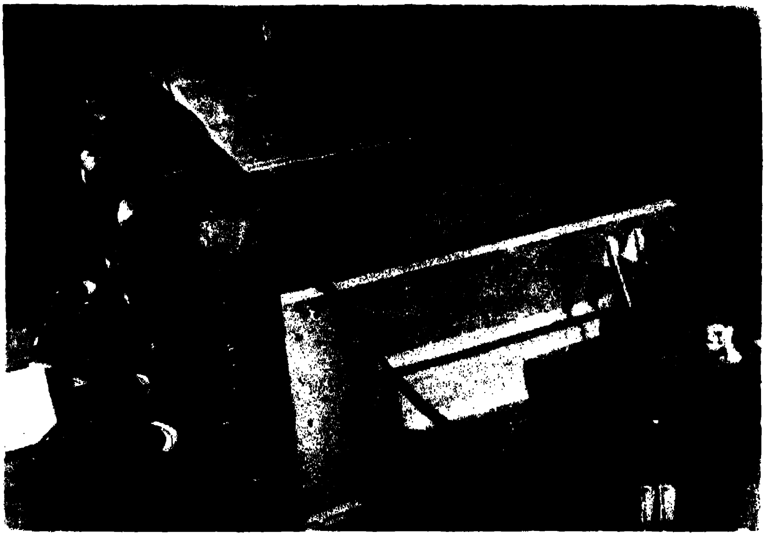

FIG. 4. A.S.R.E. Test Code set-up for self-contained air-conditioning units for comfort cooling.

The temperature of the distilled water should be kept just slightly above the wet-bulb temperature so that the bulb will be cooled quickly to its final value before the water on the wick has evaporated. One scheme for doing this, which was suggested by H. B. Slate, one of the writer's associates, is to provide a test-tube covered with a wick which can be continuously wetted from an extension leading into a beaker of water. This wick-covered test-tube is then placed in the air stream at a point where it will not disturb temperature readings and is used as the container for the distilled water. A set-up of this kind is included at the right side of Fig. 4.

Special thermometers are used which have a distance of about seven inches from the tip to the beginning of the first graduations. This is to permit the thermometer to be read without pulling it partially out of the duct. For summer conditioners it is necessary that the thermometers have graduations as close as 1/10 °F to obtain the required accuracy, while for winter conditioners where the air temperature spread is greater, $\frac{1}{2}$ °F graduations are satisfactory. Mercury-in-glass thermometers are used in preference to spirit thermometers for wet-bulb temperature readings, because they respond much more rapidly. To illustrate this point, a thermometer of each type was initially brought to 96 °F and then was dipped into water at 55 °F. In five seconds the mercury-in-glass thermometer read 61 °F, while the spirit thermometer read 76 °F.

The insulated walls of the mixing duct are extended beyond the thermometers to shield them from room radiation. The air velocities over the wet-bulbs are kept above 1500 ft/min to reduce the effect of radiation from the duct walls, which are at dry-bulb temperature. The total heat of the air and water-vapor mixture, used in making capacity calculations, is then taken to be the same as for a saturated mixture at the given wet-bulb temperature. There is a slight discrepancy between a constant wet-bulb line drawn on a psychrometric chart and a line of constant total heat starting from the same point on the saturation curve, but this slight difference tends to cancel the radiation error. It is assumed that for engineering purposes it is sufficiently accurate to neglect the two errors at velocities above 1500 ft/min.[5,6]

Experience indicates that the wet-bulb method of determining capacity for summer conditioners is generally satisfactory as far as temperature measurements are concerned. However, it has two main disadvantages. The extreme care required throughout the tests is almost more than can be consistently obtained, and in some cases the difference in wet-bulb temperature is quite small, which means that small temperature errors cause large percentage errors in the total capacity.

In attempting to measure air temperature at a given point with an ordinary thermometer a person is often confronted with the effect of radiation. For example, if a thermometer is placed near the inlet or outlet of an air conditioner, its reading is quite likely to be affected by radiation from the conditioner itself and from the room or other surroundings. W. J. King has discussed an illustration for a summer conditioner.[8] To determine how serious this might be for a winter conditioner, a mercury-in-glass thermometer was inserted in the discharge air stream of an oil-fired winter air conditioner about a foot above the center of the opening, while the conditioner was connected to a mixing box as shown in Fig. 3. The thermometer was directly over and could "see" the top of the combustion chamber. For one furnace that was tried, the thermometer read 12 °F higher than the true air temperature as determined by an aspirating thermocouple that was designed to eliminate radiation. For another furnace, which was smaller, it read 19 °F higher. When objects such as a lamp or a person's body is close to a thermometer, the reading is apt to be affected either by radiation or by the passing of the air over the object before it reaches the thermometer.

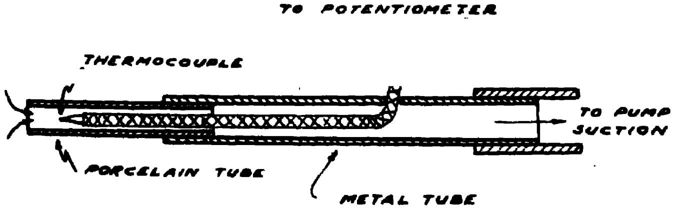

FIG. 5. Aspirating thermocouple.

So far, the discussion has dealt with temperature measurements made on the air, which tell about the overall performance of an air-conditioning system. Consideration will next be given to temperature measurements that pertain more to the equipment, and which are important in analyzing performance and efficiency.

The temperature of the flue gases leaving a furnace, or the stack temperature, is necessary in determining the stack heat losses. Thermometers which are sometimes used for reading stack temperature, particularly in field tests, read low, principally because of stem error and of radiation to the stack walls.[9] The effect of radiation can be practically eliminated by use of the aspirating thermocouple (or high-velocity thermocouple or suction pyrometer) as shown in Fig. 5. This method, which is widely described in the literature,[10] draws the hot gases at high velocity over the thermocouple, which is partially shielded from radiation. A small refrigerating compressor makes a good kind of suction pump to use, since it tends to give a constant gas flow regardless of small variations in suction line resistance. Care must be taken to insure that the gas velocity is high enough to give the maximum temperature.

Table 2 gives temperatures taken on two different furnaces, at the center of the stack. For the 7-inch stack the measurements were made a foot from the furnace, and for the 5-inch stack they were made about one and one-half feet away. The insulation used was three-fourths inch thick corrugated asbestos; and the smaller stack had a dark unfinished surface, while the larger one had a dull galvanized surface. The stem correction in this case can be omitted, since the thermometer was calibrated for 3-inch immersion. It is seen that the thermometer in the 5-inch uninsulated stack reads 65 °F lower than the true temperature and that for the lightly insulated 7-inch stack the error is still as great as 47 °F. These results for the effect of radiation on a stack thermometer are somewhat higher than those obtained in a similar manner by Nicholls and Rice for a plain thermocouple.[9] It should be pointed out, however, that this effect will vary with flue gas velocity and the size and emissivity of the thermocouple bead or the thermometer bulb.

Table 2. Comparative Readings of Stack Thermometer and Aspirating Thermocouple.

	5-inch stack bare	7-inch stack bare	7-inch stack insulated
Aspirating thermocouple (°F)	638	671	681
Thermometer (°F)	573	617	634
Difference (°F)	65	54	47

The temperature gradient across the stack varies considerably with the type of furnace. Generally, the temperature is highest at the center of the stack and falls off gradually toward the walls, giving a value of 15 or 20 °F lower at a distance about an inch from the walls. This refers to a stack covered with an inch of insulation, to a location two pipe diameters from the furnace, and to temperatures of the magnitude referred to in Table 2. However, the temperature distribution is sometimes one-sided and much different from that described. Although some type of mixing to give a true average temperature would be very desirable, yet for most purposes it is sufficient to select a point either at the center of the stack or a distance one-fourth the way across, as is specified in the A. S. H. V. E. oil-fired boiler code.[11]

Another important phase of furnace temperature measurements, in addition to that of stack temperatures, is the use of thermocouples for measuring surface temperatures. For practical purposes we usually braze the welded thermocouple bead to the point where the surface temperature is desired. As has been pointed out by Colburn and Hougen,[12] when heat is being transferred from this point to the air, the thermocouple will read somewhere between the true surface temperature and the air temperature. From tests conducted by brazing a small copper shield over the end of the thermocouple to reduce the heat transfer to the air, it appears that the unshielded thermocouple can be used on large, thick combustion chamber surfaces with sufficient accuracy for most engineering purposes, although for thin steel surfaces the error may become very large.

Thermocouples are also used extensively in checking the performance of a refrigerating system, particularly for forced-air evaporators, as is illustrated in Fig. 6. In this case they are soldered to the end turns and various other points of interest around the expansion valve and suction line. Since there is practically no heat transfer at the end turns, these thermocouples give close to the true surface temperature, which in turn is practically the same as the refrigerant temperature. More thermocouples are located toward the suction end of a coil than elsewhere, in order to determine the point where the refrigerant is completely evaporated and starts to superheat. This tells about the performance of the expansion valve, which is supposed to keep liquid refrigerant close to the end of the evaporator without permitting any of the liquid from going on into the suction line. A comparison of thermocouples on different circuits tells whether the distributor at the entrance to the circuits is working properly, while end-turn temperatures on the main part of the coil tell about general evaporator performance. These temperature measurements are used more to check up on general performance than to give accurate results for heat-transfer calculations.

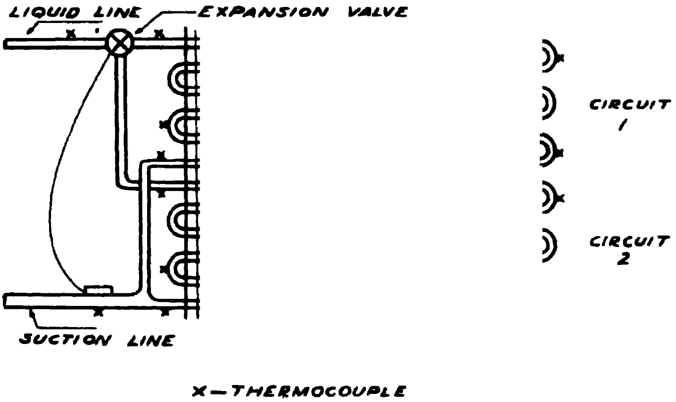

FIG. 6. Typical thermocouple locations for test on forced-air evaporator.

In developmental testing, where accurate results are required, it is necessary to make all significant temperature corrections. Except when used for high temperature or other special work, thermometers are calibrated for full immersion by comparing with a standard thermometer in a special agitated water bath. After the test data have been averaged, corrections are applied for calibration and stem error, except where the latter is relatively unimportant. For summer conditioner tests, the stem correction amounts to about 0.1 °F because of slight temperature difference between the temperature read and the ambient surrounding the stem and of the use of low-range thermometers.[10] This correction becomes much greater with higher temperatures. It may amount to between 20 and 25 °F if a full immersion thermometer is used for reading stack temperature. Another correction which is made is that caused by heat loss or gain through the mixing box. This can readily be determined from the calculated mixing-box heat loss and the air flow through it.

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Measurement of Surface Temperatures

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The growing interest in thermal engineering as a branch of applied science is accompanied by increasing problems in heat transfer and the attendant need for temperature observations. Many of these applications require measurement of heat transfer from a fluid to, or through, a solid, or vice versa. In all such problems the measurement of surface temperatures is involved. Such applications include the myriad problems confronted by the air-conditioning engineer, such as the observation of the temperature of heating surfaces in furnaces, boilers and heat interchangers. In the many heat-transfer problems dealing with building construction, it is necessary to observe the temperature of surfaces in contact with the air. More recently, the study of man in relation to his atmospheric environment has required the accurate measurement of the temperature of the human skin, either relatively dry or wet with perspiration, and in contact with the atmosphere under different conditions of temperature and humidity. The technic involved in observing temperatures of such surfaces is varied and not well standardized.

This paper calls attention to some of the practices used, some of the problems involved, and to advantages and disadvantages in their use. Its main objective is to call to the attention of investigators the need for more concentrated effort in the building up of a background of experience in such practices. so that measurements may be made with greater facility and accuracy, and so that the results may be accepted with greater confidence.

The boundary whose temperature is to be measured is usually an isothermal surface, or may be considered so for most practical purposes. In measuring the temperature of such a surface with any form of temperature-measuring instrument, it should be kept clearly in mind that all the instrument really does is to indicate the temperature of its own sensitive element, and that in order to give the results desired, it is necessary to place the sensitive element of the instrument so that it will take on the temperature of the surface. One of the first essentials, therefore, is an instrument with as small a sensitive element as possible.

When heat is transferred to or from the surface of a solid through either a liquid or gas, the mode of transfer may include radiation, convection, and evaporation. In applying the measuring instrument, care must be exercised so as not to interfere with any one of these forms of heat transfer which may be taking place. If transfer is by radiation, then the emissivity of the surface involved must not be materially affected. In most applications the sensitive element of the instrument will almost certainly have an emissivity different from the surface of the material itself, to say nothing of change in the emissivity of the surface by applying any extraneous adhesive or other means of attaching the instrument to the surface.

Similarly, since heat transfer by convection from or to a solid is affected by the area and smoothness of the surface, care must be taken that these characteristics are not altered by the application of the instrument. Again, if heat transfer from or to the surface is taking place by evaporation or condensation, this must not be interfered with; particularly, the availability of moisture at the surface must not be disturbed.

In general, surfaces whose temperatures are to be measured may be grouped into the three following types: first, metallic surfaces in contact with gases or liquid; secondly, non-metallic surfaces having fairly high electrical resistance; and thirdly, the special case of wet or moist surfaces, including the human skin, in contact with humid or dry air. The instruments used may be either a thermocouple, a resistance thermometer, or a radiation instrument.

Thermocouples have been used extensively in measuring surface temperatures. Their chief advantage lies in the fact that thermocouple wires of any diameter are readily available and the technic of their use for determining the temperature of the junction itself has been well standardized. The chief difficulty involved in their use lies in so placing the thermocouple junction and its leads that the junction will take on the temperature of the surface.

When the surface whose temperature is to be measured is a boundary between a metal and either a liquid or a gas, fairly well standardized methods of procedure have been developed. Here, the thermoelectric principle may readily be used by peening, soldering, or welding the thermocouple wires directly to the metal whose surface temperature is to be observed. Soldering or brazing, however, has the disadvantage of changing the character of the surface, particularly its emissivity. A very satisfactory practice of peening the couple into the metal was developed by Kreisinger and others[1] of the United States Bureau of Mines, in "Studies of Heat Transfer in Boiler Settings." A hole slightly larger than the wire to be used was drilled into the metal and the end of the thermocouple wire was placed in this hole through a peening tool. A single blow of a hammer on the peening tool then pressed the metal of the surface so firmly around the wire that metal to metal contact was obtained without greatly affecting the original character of the surface.

If the metal whose temperature is to be measured is such that the thermoelectric relationship between it and the wire peened into it is known, a second wire at the point of measurement is unnecessary; a lead of the same metal attached at any convenient point will serve to complete the circuit. The thermoelectric emf is set up at the point of contact between the wire and the metal whose temperature is to be measured. If the thermoelectric relation between the wire and the metal whose surface temperature is to be measured is not known, then a second wire whose thermoelectric relation with the first is known may be similarly peened into the surface any short distance away and brought out to the measuring instrument. It has been shown, both theoretically and experimentally, that a third metal between two whose thermoelectric relationship is known will not affect the measured emf, provided that the temperature of the intermediate metal is uniform between the two wires.

The one disadvantage in this application is the fact that the wires forming the leads from the thermoelectric junctions cannot be placed in the isothermal plane, and hence they will serve as an extended surface to the surface whose temperature is to be measured, conducting heat to or from it.

This method of measuring the surface temperature of metals has been satisfactorily used in the measurement of heat transfer of surfaces in boilers and boiler settings, with water, air, or flue gases as the fluid medium. Copper-constantan, Chromel-Alumel, and platinum-platinum iridium wires of 30-, 26-, and 22-gage have been used very satisfactorily. With care, wires may be thus peened into metal walls as thin as $\frac{1}{32}$ inch.

Difficulties are met with in measuring the temperatures of non-metallic surfaces. If the surface is dry and non-conducting, and if marring of the surface is permissible, the difficulty is not so great. If the surface is conducting, either by electronic or electrolytic conduction, and particularly if an important part of the heat transfer between the surface and the fluid is by evaporation or condensation, the problem becomes more difficult. Even greater difficulty is met with, however, in surfaces having these characteristics, plus the added requirement that the surface is not to be marred. Thermocouples have been most frequently employed for measuring surface temperatures under these circumstances, but some use of the electric resistance thermometer principle and of the radiation principle has been made in certain fields.

A common practice has been to place the thermocouple junction and a short length of the leads on the surface and to hold the junction firmly in contact with the surface by applying a strip of adhesive tape over it. This method has the one advantage of giving consistent results over a wide variation of temperature and surface conditions. It may be pointed out that in some types of work observations which are consistent with one another are of greater importance than the absolute accuracy of the individual reading. The obvious faults in this method are: first, the fact that the added adhesive tape submerges the junction of the couple below a new surface, adding some unknown thickness of material resistant to the flow of heat between the true surface and the fluid; secondly, the emissivity of the surface is usually altered; thirdly, the availability of moisture for evaporation is adversely affected; and fourthly, the character of the surface affecting heat transfer by convection may be altered. The total effect of these changes is to alter the rate of heat transfer between the solid and the fluid and thus to distort the isothermal plane at the very point where we want it undistorted. In order to minimize the faults mentioned above, a very thin transparent library vellum has frequently been used. The argument to justify such usage has been that the transparent film would not alter the radiation to or from the true surface and would offer only slight resistance to the normal heat flow. However, in this connection it is important to remember that a material very transparent to visible light may be practically opaque to radiation in other parts of the spectrum.

The widespread use of this method offers a good example of the need for very careful consideration of the factors involved, or better still, for careful experiments to determine the magnitude of the errors which may be introduced. Many surfaces encountered in building constructions, such as plaster, wood, pigment paints, varnishes, paper, etc., have emissivities very nearly equal to that of the adhesive tape which might be used, while the existing temperature difference between the surface and the air may be small. Under such circumstances the method might prove to result in the introduction of negligible errors.

A better practice in the measurement of such surfaces (which eliminates most of the faults pointed out above) is to make a small scratch or cut in the surface, to place the fine thermocouple wire therein, and to polish or file the wires down so that they will appear to form an integral part of the surface itself. (Sometimes plaster of paris, litharge and glycerin paste, or some similar material, is used to hold the wire in the groove, the excess binder being then filed down flush with the surface.) When making such applications of thermocouple wires to the surface, it is desirable to use as fine a wire as possible, since the finer the wire the less will be its thickness perpendicular to the surface. (Likewise the junction should be no larger than the wire itself.)

A very satisfactory discussion of the application of thermocouple wires to wall surfaces was prepared by Kratz and Broderick,[2] who showed, for a given condition of surface and air, the errors resulting from fastening thermocouples to the surface by adhesive vellum, and by imbedding No. 34 and 22-gage wire in the surface. For a 40° temperature difference between the surface and the air, errors of .5, 0, and .3° were observed respectively for the three methods of application. The errors in the first and last case were such as to indicate that the couple was measuring temperatures equivalent to those below the surface. Probably of greater value than the data cited in this paper is the method presented by Kratz and Broderick for determining the magnitude of the errors involved in any particular study.

In the observation of the temperature of surfaces in contact with air where heat is being transferred between the surface and the air by evaporation or condensation, other difficulties are involved. This condition is frequently met with in the case of heat-transfer surfaces in air-conditioning equipment. Most such cases involve metallic surfaces in which the thermocouple may be peened, welded, or pressed into the surface. However, as pointed out above, an error due to conduction of heat to or from the surface through the leads may be an important factor. In many such cases the rate of heat transfer from the solid to the fluid is so low, compared to the high conductivity of the metal, that a temperature observed from the opposite side of the metal will give satisfactory results. In applications where the thickness of the metal is a small fraction of an inch, no measurable gradient will be found through the metal. Here, obviously an observation of the temperature of the dry side will be entirely satisfactory.

In applying thermocouple wires to wet surfaces, the possibility of the moisture conducting current or setting up voltaic emfs between wires should be given careful consideration, since it will obviously affect the emf as measured at the ends of the leads. In this connection, it is well to remember that while pure distilled water is a very good insulator, the conductivity increases rapidly with the presence of minute proportions of dissolved impurities.

A surface whose temperature has been found very difficult to measure is that of the human skin. The rapid growth in the study of the relation between physiological reactions of man and his atmospheric environment has developed a very great interest in this field, so that many attempts have been made during the past few years to make such observations. An early study along this line was that by McConnell and Houghten.[3] A number of different methods of applying a thermocouple were studied; and since adhesive tape gave very consistent results without too great error, it was given some preference.

In more recent studies[4] thermocouples of fine wire with only a short length of uninsulated lead on either side of the junction were drawn or held against the exposed skin with satisfactory results. In this study, it was shown that the firmness with which the couple was held against the skin affected the temperature observed to a considerable degree. With the couples held quite loosely against the skin so that the surface of the skin was more or less tangent to the circumference of the wire, an erroneous temperature nearer that of the air was observed; whereas, if the couple were so tightly drawn against the skin that the effect was for it to lie at the bottom of the resulting depression, an erroneous temperature nearer that of blood temperature was observed. An intermediate application where about one-half of the diameter of the couple was below the surface gave what was accepted as the most satisfactory results.

In recent years the observation of the skin temperature has become somewhat of a regular clinical practice. In such cases, the physician or his technician can obviously not devote too much technical care and discretion, either to the handling of fragile, unsupported thermocouple wires, or to the nicety of their application to the skin. As a result, there has developed a widespread practice of including the thermocouple junction, or in other cases resistance-thermometer elements, in a small disk or button. This method has been used by Keeton,[5] Sheard,[6] and others. While these applications may admirably serve the purpose desired, obviously such an instrument will indicate air temperature so long as the button is in contact with the air; but when it is applied to the skin, some length of time is required before it will indicate skin temperature. On the other hand, particularly if the button is large and of such an insulating material as cork, as has frequently been used, after it is applied for considerable length of time it may indicate an erroneous temperature somewhere between the true skin temperature and that of the blood. Some comparative results of such applications are discussed in the A. S. H. V. E. Study[4] referred to above.

In measuring skin temperature it should be kept in mind that a considerable portion of the heat transfer may be by evaporation; hence, the use of a button or of adhesive tape to cover the sensitive element interferes with the availability of moisture for evaporation, and may greatly affect the results. This is particularly true in a hot, dry atmospheric environment, where the skin temperature may approach the wet-bulb temperature of the air. As an example, in air having a dry-bulb temperature of 120 or 130 °F with very low humidity, it is not uncommon to observe a skin temperature three or four degrees below the internal blood temperature of the body.

Resistance thermometers may be used to measure surface temperature. Resistance wires may be spread out to measure the temperature of an isothermal surface bounding a solid and a fluid and offers many desirable features; this method has been used to some extent in recent studies.[7,8] The obvious advantage comes from the fact that the use of the larger surface gives a well integrated effect, compared with the single point of the thermocouple junction. Here the practice has been to attach fine resistance wires of either nickel or platinum to the surface by a minimum amount of adhesive. It may be pointed out that all the elements of error attendant upon the application of thermocouple wires obviously apply; that in the last analysis all that the instrument indicates is some integrated average temperature of the wire itself; and that unless the wire is so placed that the wire will assume the temperature of the isothermal surface, errors will result. The method has been of considerable value in determining the average temperature of an imaginary plane in air in those cases where, for practical reasons, it is necessary to assume the existence of an isothermal plane. An illustration of this is in the hot-box method of determining thermal conductivity, where the basic assumption is that the air in a plane parallel to the flat surface of the box has a uniform temperature.

The chief reason for lack of confidence in the use of resistance wires is due to the lack of a long background of information resulting from experience with their use. We are all acquainted with the precision possible when using properly designed resistance thermometers. Here, however, great emphasis has been placed upon the need for avoiding strain in the wires from bending, or even by bearing the weight of more than a small fraction of an inch of the wire. These precautions have been emphasized in instances where a far greater precision is required than is necessary in the measurement of most surface temperatures. The other extreme is to wind a number of feet of suitable wire on a form and to calibrate it periodically with the degree of accuracy required. To the individual experimenter is left the choice of which method he will use. Certainly the use of this instrument offers such advantages in its integrating character that a great deal of further study directed toward devising practical equipment is warranted. One is here attracted by the wide difference in the experimental study given the usage of thermocouples by the National Bureau of Standards and many other institutions, compared with the rather meager attention given to other than high-precision usage of the resistance thermometer.

The radiation method of measuring surface temperature has been used considerably[9,10,11] and has had some careful study. The method involves the use of some form of thermopile, currently called a radiation surface thermometer, one set of thermoelectric elements of which is located in the apex of a hollow cone, the other set being maintained at room temperature. When the open base of this instrument is directed toward any surface, an emf will be observed between its leads, depending upon the radiation absorbed by the elements. For any given surface the radiation given off is a function of its temperature, its emissivity and its area. If the solid angle viewed by the receiver is entirely subtended by the radiating surface, the area ceases to be a factor. Hence, the area of the base of the cone constituting such an instrument and the angle of its side must be designed with regard to the size of the object whose surface temperature is to be measured and to the distance between such surface and the instrument. Important factors in the use of the radiation instrument itself are the emissivity of the receiving surface and the temperature of the ambient air.

The radiation method has been used to some extent to measure the temperature of wall surfaces used in building construction and to a much greater extent in measuring skin temperature. It has the obvious advantage of not in any way interfering with the character of the surface to be measured, affecting neither its emissivity, smoothness, or the rate of evaporation or condensation.

Of the several factors mentioned above as affecting its accuracy, all but the first may be dismissed as readily taken care of. The emissivity of the surface whose temperature is to be measured is, however, a most important factor, and one which is frequently either overlooked or assumed to be taken care of by the general assumption that the emissivities of the surfaces to be measured are all either unity or so near it that their variations are of no account. This assumption has grown up in the consideration of heat transfer through building construction, and it is probable that any error in the assumption has little effect for that usage. However, even a relatively small variation in the emissivity of the surface whose temperature is to be measured may be an important factor in the determination of that temperature with a radiation instrument, and it has been adequately proved that the variations in emissivity of plaster, wood, paper, pigment paints, varnishes, clothing, and the human skin, while not very great, are frequently sufficiently lower than unity that compensations must be made.

The effect of the relative size of the surface whose temperature is to be measured and the size, shape, and location of the sensitive element of the radiation instrument also need some consideration. These will obviously depend upon the design of the receiving cone. Before using such an instrument promiscuously in measuring the temperature of any surface, the observer should acquaint himself by experimental observation with the solid angle of view which determines how far it may be held from a surface of a given size; otherwise, erroneous results may be obtained caused by including in the angle of view other surfaces having different emissivities or temperatures. In general, the emphasis should be placed upon the maximum distance from a surface of a given area at which the instrument may be held. In some instances, however, care must be taken not to hold the instrument too close, since if the opening of the cone is held too close to a surface whose temperature is considerably different from that of the sensitive element, convection currents may enter the cone and affect the observations.

In discussing the subject of measuring surface temperatures the authors wish again to emphasize that their purpose has been largely to draw the attention of the physicist and instrument designer to the need for improvement in methods and practices in measuring surface temperatures as an important factor in the advancement of our knowledge of heat-transfer studies.

Discussion

H. T. Wensel, National Bureau of Standards: There are several methods of measuring surface temperature not discussed in this paper but covered in other papers of this Symposium, among which are methods based on radiant energy emission, discussed by W. E. Forsythe; interferometer methods by R. B. Kennard; and thermoelectric methods, in which provision is made for improving thermal contact and reducing the heat loss from the junction, discussed by W. F. Roeser.

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The Measurement and Control of Temperature in Refrigerator Cars

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The measurement and control of temperature in refrigerator cars presents a special type of problem, in that certain restrictions must be put upon the methods employed. Perhaps the most important of these restrictions is that of simplicity. Complicated apparatus and equipment are entirely out of place on a freight car.

The railway systems of North America cover thousands of miles and pass through regions where neither instrument makers nor specialized mechanics are available. If complicated equipment were to need repair, this could not be done until the car reached a point at which trained repair men were available. On the other hand, simple equipment could be attended to by the railway's own mechanical men, if repairs were necessary en route.

Furthermore, economic considerations prevent the railways from spending large sums of money on accessories. Accessories must be justified either by an increase in tariff or by an increase in business. Elaborate means of measuring and controlling temperatures in refrigerator cars are hard to justify.

Equipment designed for service on freight cars must be rugged enough to withstand the severe shocks occurring when cars are shunted. Each car must be a complete unit, so that interference with the operation of making up trains at divisional points does not occur. Thus a "master car" carrying heating or cooling equipment for several others cars is not a satisfactory solution.

The equipment must withstand extremes of both heat and cold. Temperatures in cars standing empty on sidings in summer may rise to 120 °F. Equipment located outside the car has to be protected against drifting snow and sleet. Control apparatus and means for making adjustments must be designed for use by non-technical men, and must be operated from outside the box of the car.

Electrical power cannot be supplied, hence any electrical equipment must be operated by primary batteries. Steam under pressure is not available. Mechanical power is available if use is made of an axle drive, but railway authorities do not favor the use of this source of power.

In recent years biologists have concluded that accurate temperature control is desirable for certain products. If a product is to be carried by rail from the western to the eastern coast, the trip may require about nine days, which is a long time for a product to be held at an incorrect temperature. If the best results are to be obtained, and if the confidence of the shipper as to the safety of his product is to be won, the aim should be to control refrigerator-car temperature within a few degrees, throughout the trip. In the case of an item such as celery, some authorities have felt that still finer control is desirable.

The equipment in use at the present time on railroads is hopelessly inadequate for control of temperatures. This may be evident from the history of the equipment. An ordinary box car formerly had its walls, roof and floor insulated and ice was put in bunkers at the ends of the car. When heat was needed, charcoal heaters were lowered into the ice bunkers. When the car required ventilation, the hatches of the ice bunkers were opened slightly. A false floor was provided which allowed air to circulate under the lading. Methods were introduced for stacking commodities so as to take advantage of air circulation. The ice bunker was improved and at present the divided basket bunker is favored. There is no need to go into the details of all the improvements on doors, floor racks, heaters and methods of insulating the walls; it suffices to say that while the modern refrigerator car is exceedingly well insulated, the methods of supplying heat and cold are unsatisfactory.

Indeed, one rather wonders at the present relative efficiency of the system, since the principles on which it works are fundamentally bad. The bunkers are so constructed that cold air from the ice flows out at the bottom, along the car under the load, then up through a space left open in the load at the doorway, and finally back above the load to the bunker. When the car is being heated, the hot air rises in the bunkers, fills the empty space above the load, then it passes down through the load or through the open space at the doorway and finds its way back to the bunker along the floor. The present design of bunker permits cold air to flow to the bottom of the car and hot air to flow to the top. In either case, it provides the ideal conditions for establishing high temperature gradients. With the present equipment it is therefore impossible to maintain a uniform temperature throughout the load. If the temperature is controlled correctly at the top it is incorrect at the bottom, and vice versa.

To overcome this serious defect, the top-bunker car with underslung heater has recently been developed. On this car, the ice bunkers are situated above the load so that cold is supplied in the right place. An inner wall permits the cold air to flow down the side of the car and thus to blanket the car with cold air.

Due to the removal of the ice bunkers from the ends of the car it was necessary to find a new location for the equipment for heating the car in winter. The old method of locating heaters in the end bunkers was fundamentally wrong, as heat should be supplied to a car from underneath the load. To accomplish this the underslung heater was designed. This is attached to the car underneath the floor. A coiled pipe passes through the source of heat and is connected to a circulation pipe lying under the false floor of the car. There is sufficient height between the floor and the rail to permit gravity circulation. Antifreeze liquid is used in the circulation pipe so that freezing will not occur when the car is out of service in winter.

This type of bunker-equipped car is thus cooled from the top and heated from the bottom. Temperature gradients are therefore negligible. By varying the amount of salt used in an ice and salt mixture, various degrees of refrigeration can be obtained, but control of the heat supply is a more difficult matter.

Before discussing the control of the heating equipment it is necessary to consider the methods of measuring temperature inside a refrigerator car. In the ordinary refrigerator car in service there is no ready method of ascertaining this temperature, as the doors are sealed. One might then ask, "how do railway employees know when to light the heaters which they place in the end bunkers?"

This is done by consulting a schedule based on the outdoor temperature. During a long trip, such a system is dangerous because if the schedule for a particular product demands that heaters be lighted when the temperature falls below 15 °F, and the temperature happens to range from 16 to 28 °F for four or five days, the heater is not lighted and the cold eventually creeps through the walls and damages the load.

It is necessary to have a means of knowing the temperature inside the car, to make accurate manual control possible. This requires some sort of distant-reading thermometer, such as the well known liquid expansion pressure-spring instrument, preferably of the fully compensated type. One bulb is placed under the floor racks and another close to the roof of the car. On the side of the car there are two dials, and on these the two temperatures are read. By means of this arrangement the conditions inside can be seen at a glance. The readings show not only the two temperatures but also the magnitude of the temperature gradient between the top and bottom of the car.

For ordinary service, one temperature taken at the top of the car and one taken at the bottom are sufficient, but sometimes with experimental shipments temperatures at other places or in the load itself are required. A resistance thermometer is suitable for this purpose.

So far the thermocouple, in spite of its simplicity and the ease with which it can be inserted into boxes, has not come into use. However, it is of interest to note in passing that at the Ditton Laboratory in England the resistance thermometer gave place to the thermocouple for measuring temperature in their model ship's hold. It seems probable that the thermocouple would be suitable for readings on experimental shipments in refrigerator cars, if proper attention is paid to the reference junctions.

If a car is equipped with an underslung heater and distant-reading thermometers, it is possible to control the inside temperatures in a manner satisfactory to shippers. Splendid results have been obtained with outdoor temperatures ranging from 30 above to 30 below zero Fahrenheit.

Two forms of underslung heater have come into use. One is a heater burning charcoal, which is used by the Canadian National Railways on several hundreds of their refrigerator cars. The other is a gas heater favored by the Canadian Pacific Railway. The charcoal heater is controlled with adjustments of the draught, while the gas heater is controlled with a valve in the gas line. The gas heater would appear to be the more adaptable to automatic control, but so far neither heater has been used in general service satisfactorily without manual adjustment. Although manual operation has given some very good results, automatic control is to be preferred. With manual control, if a car inspector should make a mistake or an error in judgment the heater would be sent off wrongly adjusted perhaps for an eight-hour run, during which time the temperature inside the car might change considerably.

In order to control a damper a thermostat must have considerable power. Experiment has shown that it is not sufficient to control only the outlet for the fumes, but the air supply must also be controlled. Since electrical power is not available, and since use of the air-brake compressed air supply is undesirable, the most feasible thermostat seemed to be one depending either on the expansion of a liquid or on the bending of a bimetallic strip.

A thermostat operating on the principle of liquid expansion was designed and tried on a refrigerator car with some measure of success, but the apparatus involved was more complicated than anticipated.

Indications to date show that the bimetallic coil offers better possibilities. In the laboratory a bimetallic coil made from a band 3 inches wide and $\frac{3}{8}$ inch thick has been set up and made to operate a damper. No trouble whatever was experienced in obtaining adequate movement of the damper, and a coil of this type was said by the manufacturer to be able to withstand the strain of 120 °F. Experiments on a refrigerator car with this thermostat are at present in progress, and if the damper's movement is not affected by the weather, prospects appear excellent.

With a control which operates a damper, the fire must be extinguished when mild weather is encountered. The automatic arrangement is then out of action until the fire is relighted. Thus under certain weather conditions a damper control is not fully automatic. It has been suggested that a by-pass valve on the circulation system, operated automatically, be used to prevent any heat from entering the car when the weather is mild. A difficulty lies in finding a thermostat with sufficient power to operate the required valve. The use of a relay valve seems essential, and work is at present in progress developing what might be termed a thermal relay. The thermostat used for operating the damper is expected to operate a flap which, when open, permits hot air to strike a sylphon bellows containing a volatile liquid, and arranged to operate the valve. The use of such a relaying device, however, adds a complication in design.

The gas heater equipped with a pilot light, seems to have an advantage over the charcoal heater when complete automatic control is considered, because the thermostat needs only to control the supply of gas. The heaters supplied to the Canadian Pacific Railway were equipped with a thermostat which depended for its operation on the change with temperature of the vapor pressure of a volatile liquid. The results obtained in service were not good, and it is understood that the Canadian Pacific Railway had to revert to manual control.

In summary, automatic control of temperature in refrigerator cars is still a live problem of considerable commercial importance. The fact that manual control with the aid of distant-reading thermometers is a tremendous improvement on the general practice of using the end-bunker heater and estimating the temperature in the car from the outdoor temperature, retards the development of the automatic heater. Railway companies are naturally reluctant to spend money on further developments until shippers appreciate the better service which is being afforded already by the underslung heater. There is, however, a definite trend toward such appreciation.

Temperature Measurement and Control in the Food Industry

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Basis of the Problems

The problems of temperature measurement and control in the food industry can be seen in best perspective by considering the industry itself for a moment.

We have been reminded of the importance of food in the flood of recent comments on the war, and it is almost trite to say that the progress of civilization and the development of the food industry are so closely allied as to be different aspects of the same phenomenon—the increase in world population.

Man conquered his first problem of existence when he learned how to store food and make it available regardless of season. This was the birth of the food industry of today—a process of smoothing out the feast-famine cycle. Grain was important to the ancients because of its inherent stability under easily achievable conditions.

Almost all the temperature control and measurement problems of the food industry stem from the one thought, "achievable conditions." As examples, root cellars and heaps of apples covered with straw were the precursors of our modern cold-storage warehouse. The canning process of Nicholas Appert is the storing of sterile food in hermetically sealed containers.

The development of the industry is proceeding at an accelerated rate. This is in answer to the increasing demand made on it, such as that caused by the findings concerning vitamins, and the recognition of deficiency diseases. The industry is meeting these challenges, and it may be said that preserved foods today supply vitamins in satisfactory amounts.

Scope of the Problems

In its broad scope and diversity the food industry has been forced to solve numerous types of temperature control and measurement problems. Many of the subjects presented in this symposium bear on this industry. The diversity becomes evident from an analysis of its various phases.

The industry can be generalized into four stages:

(1) Raw materials storage and shipping.
(2) Preparation and treatment of the raw material.
(3) Processing: canning, sterilizing, freezing, preserving, converting.
(4) Storage and shipment of finished product.

These stages can be broken down into typical conditions of temperature measurement and control:

(1) Air temperature:

    a. rooms
    b. ovens
    c. dryers
    d. refrigerators.

(2) Liquid temperatures:
- a. pipes
- b. tanks, fermenters
- c. heat exchangers.

(3) Steam temperatures:
- a. retorts
- b. steam jackets
- c. steam coils.

(4) Temperature of dry media other than air: a. grains.

There is no difficult or unusual problem in this list. All are commonplace, and in general, thermometers and controllers well suited to the tasks are available.

The temperature range is not wide. Temperatures below −40 °F and above 500 °F are rarely met, while the most common range is from 0 to 270 °F. A rough classification follows:

Operation	Range (°F)
Quick Freezing	0 to −40
Freezing Storage	0 to 32
Cold Storage	32 to 50
Room Temperature	50 to 100
Pasteurizing	120 to 212
Flash Pasteurizing	160 to 240
Sterilizing Foods	212 to 270
Roasting	300 to 500

Under all these conditions certain general principles apply.

Principles Underlying Temperature Control

Storage of Food

We ask your indulgence while we repeat, for the benefit of the personnel of the food industry, that thermometers do not indicate the temperature of the medium surrounding their bulbs, but rather the temperature of their own sensitive bulbs. It is true that these bulbs generally have practically the same temperature as the surrounding medium, but this distinction is commonly overlooked by non-technical minds.

In the temperature control of storage conditions for raw materials or finished products, the degree of sensitivity of the bulb of the controller is not especially important. Fluctuating temperatures usually are not required as part of storage conditions, and when temperatures do fluctuate, any thermometric lag in response by the sensitive element is not sufficient to affect those conditions materially. The location of the element with respect to that of the materials being stored may be important if the materials, when placed in storage, are at a temperature differing considerably from that of the storage room. Also, if the materials are placed compactly, the time required for the interior portions of a compact mass to reach the temperature of the room may be so great that the quality of these portions of material may be seriously impaired by the abnormal temperatures.

It is usually impracticable to place a bulb at a slowly heating or cooling point within a compact mass of material. Even if a bulb were so placed, it would be impracticable to base the control of temperature on its indications because, in such a case, the material in exterior portions of the mass (which would be the largest portion of the material) would be adversely affected by abnormal temperatures imposed as a result of the effort of the controller to establish normal storage temperature at the bulb. Therefore, to maintain proper storage conditions, it is necessary first to maintain proper temperature at a chosen point, secondly, to maintain air circulation, and thirdly, to arrange the material carefully to insure that the circulation will be effective to all parts of the material so that the prescribed temperature of the controller element is assumed by the material as uniformly and expeditiously as possible.

The important part of the storage temperature control problem is to determine what the proper storage temperature is and how to arrange the material in storage so that all parts are subjected to the prescribed temperature throughout the storage period. This information is usually best obtained through laboratory experiments by studying effects of different temperatures upon food, and rates of heat penetration into compact masses of the food held under different conditions of air circulation. After the necessary information has been obtained, its application to commercial conditions is usually a simple matter.

Processing of Food

The application of temperature control to processing operations is a more difficult matter, since somewhat precise time-temperature cycles are involved, and consequently, the phenomena of heat transmission and heat penetration become highly important factors.

In processing, whether it be of smoked, salted, spiced, pickled, dried, frozen or canned food, the more severe or extreme the processing conditions, the more difficult is the control operation. The most drastic processing conditions, in the intensity of their effects on food, are to be found in the sterilization of canned food by heat. Essentially, a sterilizing process consists of heating the food to a specified temperature in a specified time, holding at a specified temperature for a specified time, and cooling in a specified time.

A sterilizing process may be either by continuous or by batch procedure, and completely automatic control is possible in either case. Continuous operation consists of passing food, either in bulk or in containers, continuously through a heating and cooling apparatus. The control mechanism is less complex when processing is continuous than when it is carried out by batch operation. In continuous operation, the essential factors in control are first, maintenance of proper temperatures continuously in the heating and cooling media which make contact with the food or food containers, and secondly, maintenance of constant rate of flow of food through the apparatus. In batch operation the essential factors are first, control of rise of temperature of a heating medium, secondly, maintenance of proper temperature continuously in the heating medium during a holding period, and thirdly, control of fall of temperature of a cooling medium. All these control operations must be carefully manipulated with respect to time.

As in storage, before a processing operation can be carried out, the conditions that are to be maintained must be determined by laboratory tests. The determination of these conditions for canned foods processes is a complicated procedure. It involves first, discovery of the temperature conditions that will sterilize the food, and secondly, learning how the necessary temperature can best be introduced into the food. In the first phase of the study it is usually necessary, or at least desirable, to find the temperature conditions that sterilize while producing the least change in edible qualities of the food. In the latter phase of the study, heat penetration tests of cans of food play an important part if the food is to be sterilized in the can. If bulk sterilization is to be carried out, the temperature of the food in different parts of the system while the food is moving continuously must be measured. Knowledge of the temperatures of different portions of the food while it is passing through a process is necessary in order to establish the manner in which the process will be carried out.

Examples of Processing

Food in Containers

To gain an insight into these temperature differences let us take the most prosaic example possible—a can of beans being prepared for market.

This product is too heavy in consistency to permit the flow of convection currents, and in common with many foods has a thermal conductivity about equal to water. In its preparation it is heated in a kettle to about 180 °F and is then placed in a small steel cylinder or can and hermetically sealed. It must then be sterilized. Through a combination of experience and bacteriological research it has been found that harmful or spoilage-producing organisms cannot survive if the beans and sauce are maintained at 250 °F for three minutes, 240 °F for twelve minutes, or 230 °F for fifty-five minutes. These data describe a thermal death-time curve and fall approximately on a straight line on semi-log paper.

The can must be heated till all points in it have received sufficient heat treatment to satisfy the demand of this thermal death-time curve. This is done by placing the can, with a host of others, in a steam retort—a pressure cooker.

We pause a moment to consider two important general factors in their influence on the problem. One is the heating (or cooling) medium. In canning, steam is used because it is the fastest. Each bit of water vapor gives up its heat, condenses, and so gets out of the way for the next particle. Water approaches steam in effectiveness when its rate of circulation becomes extremely great. At low rates of circulation of water the decrease in heating compared to that of steam is very noticeable. Air is a very poor medium in comparison and also varies in effectiveness with its rate of circulation. The other general factor is the object being heated or cooled, in this case a can of beans.

As the steam is admitted to the retort the outside of the can becomes heated. The retort is brought to temperature—say 250 °F (15 lbs. steam pressure)—and the period of holding starts. A thermocouple at the center of the can would show no immediate rise in temperature. The heat wave has started into the can, but since it travels by conduction through a water-soaked mass, its movement is slow. In fact, if the can had been held at room temperature between the filling and the start of the process, so that the outer layers of the food cooled somewhat, the center temperature would drop after the process begins, and before the heat wave reaches the center. After the center temperature has started to rise under the full impulse of applied heat, it continues to rise, traversing a constant fraction of each successive remaining temperature interval (retort temperature minus can-center temperature) in unit time.

The heating curve thus has two significant characteristics:

(1) A time lag which measures the time taken for the full force of the heat wave to reach the can center. The larger the bulk, the longer this time; thus for a cylinder of a heavy sauce-like material, 2″ in diameter by 4″ high, it takes approximately six minutes; for one 6″ in diameter by 12″ high, about 55 minutes; and if we had a cylinder 48″ in diameter by 96″ high, it would take about 3,450 minutes for the wave to reach the center.

(2) Asymptotic approach to retort temperature after the heat wave reaches the center. For the three cylinders the times to traverse 90 per cent of the temperature interval are:

2" diameter × 4" high	27 minutes
6" diameter × 12" high	240 minutes
48" diameter × 96" high	15,180 minutes

The presence of free-flowing convection currents can reduce these figures to less than one-tenth of these values, and if the product is of a dryer nature the figures may be doubled or trebled.

After the can of beans has been properly heat-treated, the steam is shut off and water used to cool it. The can center will show a lag in responding to this treatment exactly as in the heating, and the center may continue to rise temporarily despite the surrounding cold water. The cooling curve is approximately similar to the heating curve.

The mathematical calculations as to the length of the process, and the theory of heat penetration have been well covered in the literature.[1,2,3]

Food in Bulk

One of the most interesting cases of temperature control encountered, is in the continuous blanching of peas in tube blanchers. This operation consists of heating the peas in water to a selected temperature between 160 and 212 °F for a period of three to ten minutes, depending upon the requirements of the canner. The blanching water is circulated continuously, and the temperature of the reservoir is maintained near the blanching temperature. The blanching operation takes place in pipes about three inches in diameter. The raw peas at room temperature are mixed into the water and the mixture flows through the pipes. At the end of the blanch, the peas are screened from the water, and the water is returned to the reservoir. The flow of the peas is uneven and usually intermittent. The weight of the peas is from $\frac{1}{10}$ to $\frac{1}{3}$ that of the water. The solution of this problem lies in permitting the cold peas-hot water mixture a short period of temperature equalization before it passes the main temperature-control bulb. Since the drop in temperature of the mixture is proportional to the steam demand, the controller should be a throttling type which adds approximately the correct amount of steam to raise the temperature of the mixture to the desired point. The steam inlet is located just far enough beyond (downstream) the sensitive element to compensate for the delay in action of the controller. In this way the required amount of steam is added to that part of the mixture which caused the controller to act. A second similarly installed controller located farther along the pipe serves further to smooth out temperature variation and an even blanching condition is maintained. The necessity of the second controller lies in the variation in size of the peas. A mixture of hot water and small peas comes to equilibrium faster than a mixture containing large peas. The difference of heat penetration into the peas themselves is thus compensated.

A few general suggestions may be of value.

When a point temperature is required in a non-agitated medium, great care should be taken to prevent agitation by the element itself.

In all cases the heat conduction of the stem to the bulb should be as low as possible. Lack of observance of this principle is a common source of error. This factor is usually more important in the control of a gaseous than of a liquid medium, especially if the disturbing temperature condition in the stem is imposed by a liquid or liquid-vapor medium.

The location of the sensitive element should be carefully chosen, so that the instrument measures the temperature desired. The element must be free from local disturbances.

In agitated media, the more rapid the agitation the better the response. It often makes for better control to divide the load (heat added or subtracted) into a static and a fluctuating load. The static portion is not controlled, but is set at a constant value. Thus in a gas-heated baking oven a by-pass hand valve is set to maintain the empty oven at or near the desired temperature, whereby the controller needs to compensate only for the baking goods introduced. In this way over-control and "hunting" are more readily avoided.

With fluctuating temperatures: (1) the heat capacity of the sensitive element should be as small as possible. (2) The surface/mass ratio of the element should be as large as possible. With steady temperature, these lose their importance.

Summary

This paper expounds some of the principles on which successful temperature measurement and control in the food industry depend, and avoids dwelling on details of the application of the various types of instruments used, with the endless exposition entailed in such a task.

With the assistance of laboratory tests, proper temperature control conditions for a given operation in the food industry and a specific manner of attaining those conditions can be readily established by an engineer having a knowledge of the principles underlying temperature control. Often, this can be accomplished even before it has been decided whether the control will be manual or automatic.

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Temperature Measurements with Probes of Large Mass in Stoker Fuel Beds

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During the winter of 1937-38, measurements of temperatures and gas compositions at various points in the fuel bed of a large underfeed stoker in the Hell Gate Station of the Consolidated Edison Company of New York were made as part of a coöperative research project undertaken by the Company, the Coal Research Laboratory of the Carnegie Institute of Technology, and Bituminous Coal Research, Inc. A preliminary report of the results of these tests was presented at the Annual Meeting of the American Society of Mechanical Engineers in December, 1938, where it was pointed out that a final report could not be made until some of the observations had been corrected. The present paper describes the work done in arriving at those corrections and demonstrates the method of applying them. The need for corrections arose from the fact that the limited life of the probes used in the tests made it impractical to allow time enough for the probe to come to temperature equilibrium with the bed in the early stages of each run. The corrections made possible the estimation of the actual temperature in the bed at points reached early in the run from the observations of temperature and of the time rate of rise of temperature indication at the point.

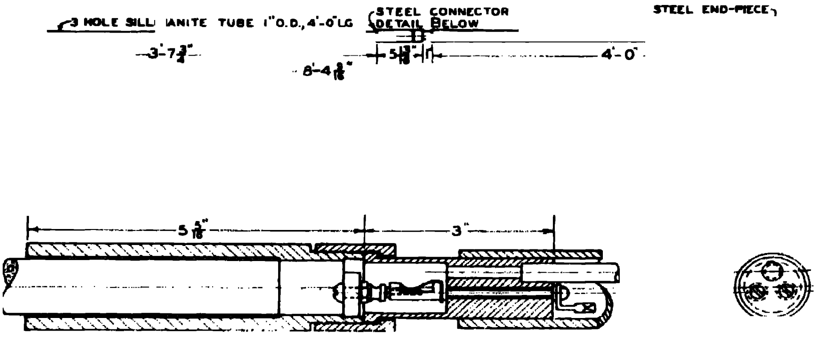
3 HOLE SILLIMANITE TUBE 1"O.D., 4'-0"LG
STEEL CONNECTOR DETAIL BELOW
STEEL END-PIECE
3'-7¾"
8'-4⅛"
5⅜"
4'-0"
5 1/16"
3"

FIG. 1. Probe assembly and detail.

In the fuel-bed tests, probes of heat resisting material were passed up through holes in the stoker iron into the fuel bed at eight points in a tuyere stack and in the retort adjacent to it. These probes were made of mullite and had three holes: one, $\frac{1}{8}$ inch diameter for drawing a gas sample; and two, $\frac{1}{16}$ inch diameter for thermocouple leads. Because of the high mechanical stresses to which the probes were subjected, it was necessary to make them one inch in outside diameter. The probes were fastened into iron-pipe extensions by which they were manipulated from the working place below the fuel bed. A drawing of the probe assembly is shown in Fig. 1.

When the probes were first used in the burning lanes, where temperatures up to 3000 °F are encountered, accompanied by considerable amounts of slag from the melted ash of the fuel, it was found that the probes failed by thermal shock after very short exposures, and that the thermocouple hot junctions frequently were attacked by the slag. The contamination from the latter source manifested itself by the appearance of millivoltages corresponding to temperatures considerably greater than the melting point of the platinum wire. In order to overcome these difficulties, a silica sleeve was cemented to the upper end of the mullite probe so that it projected ⅛ inch beyond the end of the mullite, and a cap of Alundum (commercial aluminum oxide) and Insalute, a commercial refractory cement with a sodium silicate binder, was cemented over the thermocouple junction in the cup so formed, leaving an opening over the hole through which the gas sample was drawn. The cap was allowed to dry for two or three days, and was then heated to a temperature of 800 °F in about 8 hours and allowed to cool slowly. This procedure produced probes which were uniformly effective in penetrating from 8 to 15 inches into the fuel bed before failure. A photograph of one of the completed probe ends is shown in Fig. 2. The probes used in the retorts did not undergo such drastic treatment and, since it was desirable to keep the thermal capacity of the probes as small as possible, they were not equipped with the sleeve or cap.

FIG. 2. A probe end before assembly with the holder, showing silica sleeve and cemented cap.

In view of the large volume of material at the end of the probe, it was anticipated that the probes would show some lag in reaching fuel-bed temperatures, and, in the early tests, probes were held in position until the rate of increase of the indication dropped to 0.1 mv in a half minute. This was, however, very time-consuming and tended to cause premature breakage of the probes; later on, therefore, the probes were held at each position for 2½ minutes, readings being taken every half minute. This allowed time enough to secure the other readings and a gas sample at the point, but quite obviously introduced the necessity of finding a method of predicting the fuel-bed temperature from the observations when a steady indication was not reached. A portion of the log of a typical run is shown in Table 1, starting with the insertion of the probe to its initial position, 1 inch below the level of the tuyeres on which the bed of burning fuel rests. From this point the probe was advanced by ½-inch steps up to a point 5 inches above the level of the tuyeres, and from then on by 1-inch steps. The portion of the log shown follows this up to a level only 4 inches above the tuyeres, but the remainder of the log is not essentially different from that shown in the table. It will be observed that at each point below position 28½, 3 inches above the level of the tuyeres, the temperature indica-

Table 1.

Run No. 72

No. 2 Tuyere, East

Zero = 25½"
March 25, 1938

Time	Position (inches)	Potentiometer Reading (mv)	Temp. (°F)	Bed Differential	Sample No.
2:19	24½	0.8		2.05	
		1.1			
		1.3			
		1.4	385		
2:21	25	1.7		1.0	
		1.7			
		1.7	450		
2:22	25½	1.6		0.44	
		1.6			
		1.7	450		
2:23½	26	2.1		0.44	43
		3.3			
		4.2			
		4.6			
		4.9	1055		
2:25½	26½	5.0		0.43	16
		5.4			
		6.0			
		6.4			
		6.8			
		6.9	1400		
2:28	27	7.1		0.47	17
		7.6			
		8.4			
		8.8			
		9.3			
		10.0	1900		
2:31	27½	10.5		0.55	18
		10.7			
		12.2			
		12.5			
		12.6	2295		
2:33½	28	12.9		0.60	19
		13.2			
		13.9			
		13.8	(13.9)		
		13.9	2490		
		14.0			
2:36	28½	14.2		0.59	20
		14.2			
		14.2	(14.0)		
		13.9	2505		
		13.8			
		13.7			
2:38½	29	13.6		0.90	21
		13.6			
		13.6			
		13.7	(13.8)		
		14.1	2475		
		14.1			
		14.1			
2:42	29½	13.9		0.80	22
		14.1			
		14.2			
		14.3	(14.2)		
		14.4	2535		
		14.2			
		14.1			

tion rose continuously throughout the time the probe remained stationary. In fact, the rate of rise of observed temperature at the end of a period was, in one case, as much as 0.7 mv, corresponding to more than 100 °F, in a half minute. From position 28½ on, however, the temperature indication rose and fell in an irregular fashion within a fairly small range at any one position. The appearance of fluctuations of this order of magnitude in the observed temperatures suggested that the probe had reached equilibrium with the fuel bed and was following its fluctuations with, perhaps, a lag in phase and somewhat diminished amplitude. In the upper part of the fuel bed, beyond the portion shown in the table, the fluctuations diminished in magnitude and the temperatures appeared to be nearly steady, at least over a 2½-minute period of observation.

Evidently, the continuous rise in temperature indication was due, not to any change in the temperature of the fuel bed in its lower portions, but to the lag of the probe in reaching equilibrium with the bed. This diagnosis was confirmed when, on one occasion, it became necessary to withdraw a probe from the bed very abruptly after it had reached a temperature in the neighborhood of 2000 °F. After 17 minutes, the thermocouple still indicated a temperature of 590 °F although it had been exposed to room temperature all the time.

In retort tests, the temperature remained constant at room temperature to a level of 20 inches or more above the level of the retort bottom, but then increased within 2 inches to above 2000 °F. Here, again, it was impossible to secure stationary readings, but in this case the difficulty was complicated by the fact that it was probable that the temperature of the fuel bed itself was increasing at each point, and it was impossible to separate the effects of the probe lag from those of the heating of the bed. Thus it became necessary to secure reasonably precise information about the behavior of the probes when suddenly exposed to a source at a high temperature.

Experimental

The first tests of the probes were made by plunging them into a box of granular coke in a gas-heated muffle furnace after the coke and furnace had been heated to 1800 °F. The results of these tests duplicated approximately the temperature history curves obtained in the fuel bed by leaving the probe in place at one position in the retort. These results were, however, difficult to analyze, although they were not dissimilar to the temperature history of a semi-infinite solid heated at one face.[1] It was decided, therefore, to test the probes in model fuel beds representing as nearly as possible the conditions of use, and to compare their indications with those of thermocouples mounted in holders of negligible thermal lag. This necessitated making tests under two different conditions, one representing the conditions above a tuyere stack, and one representing conditions in a retort.

The first case was set up with the aid of the U. S. Bureau of Mines Pittsburgh Experiment Station who made available one of their experimental furnaces previously used for a study of underfeed combustion. Short probes of mullite were made up with silica sleeves and cemented caps in exactly the same way as those used in the stoker tests. These were mounted in the experimental furnace as shown in Fig. 3. At the level of the tip of the probe, a thermocouple in a 2-hole porcelain tube ¼ inch in diameter, without a cap, was inserted from the side of the furnace to within 2 inches of the tip of the large probe. The use of an uncapped probe necessitated the use of a practically ashless fuel to avoid contamination of the thermocouple junction. This condition was satisfied by the use of petroleum coke, a supply of which was available at the Experiment Station. The small probe was brought in from the side of the furnace because it reduced the probability of error in its indi-

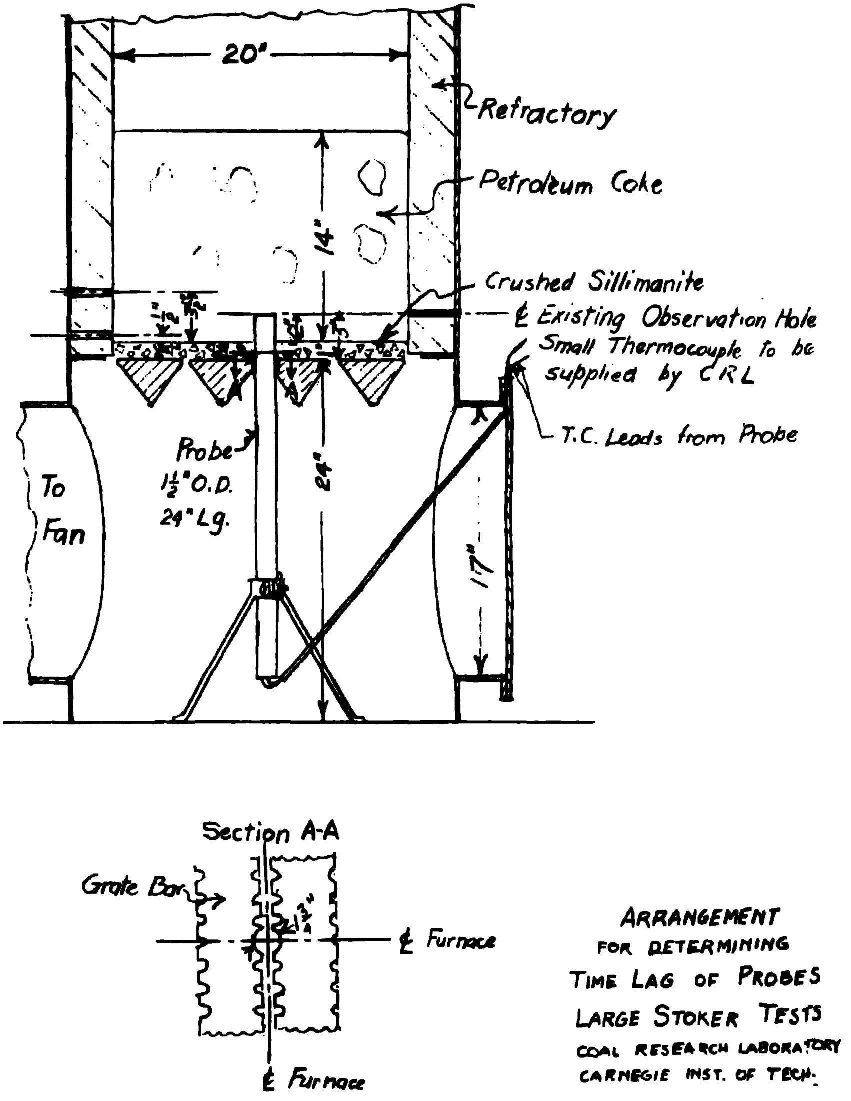

FIG. 3. Pot-type furnace arranged for testing capped probes.

cation due to conduction along the couple, as horizontal planes are nearly isothermal surfaces in this apparatus.

The procedure in the tests was as follows: The pot-type furnace was filled with crushed petroleum coke to a depth of about 15 inches, requiring about 70 pounds of coke. The probe and the auxiliary thermocouple were then installed to marks which insured that their tips were at the same level within $\frac{1}{8}$ inch and were not over 2 inches apart. The thermocouple leads were brought to Dewar flasks containing an ice and water mush, from which copper wires led to the potentiometer, so arranged that it could be switched to either thermocouple. The fire was lighted at the top by igniting about 5 pounds of charcoal soaked in kerosene spread on top of the bed of petroleum coke. The fan was started and increased in speed slowly as the fire took hold, to the predetermined rate of air flow, which was measured by an orifice meter. Occasional readings of both thermocouples were made, as well as observations of the rate of advance of the plane of ignition through the bed of fuel, until the auxiliary probe showed the first departure from room temperature. Thereafter, both couples were read as frequently as possible until the very rapid increase that first appeared was checked. Thereafter, the couples were read at increasing intervals until the fire was burned out, or until both couples failed. The small couple always failed after 15 minutes to a half-hour. This procedure was carried through for tests at two different air rates, 200 and 400 lbs/sq ft/hr, and with two different positions of the probe, at levels ½ inch and 2 inches above the bottom of the fuel bed. A graphical log of a typical run is given in Fig. 4.

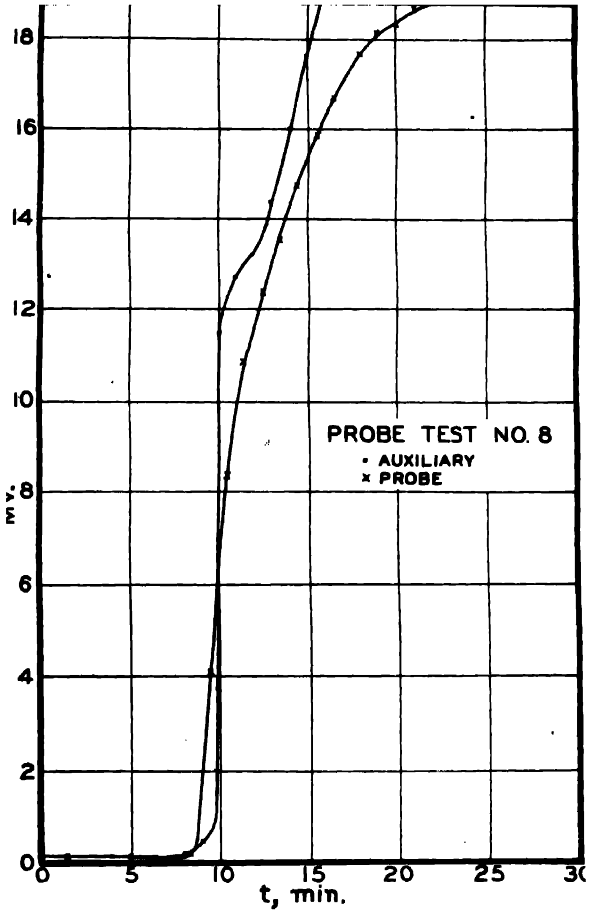

Fig. 4.

Log of probe test No. 8 made in pot-type furnace.

In order to represent conditions in the retort, it was desirable to heat the fuel bed from one side, and to pass as little air as possible through the bed. An attempt was made to do this in the pot furnace by igniting at the top and allowing it to burn down without supplying primary air under pressure, but the fire did not remain ignited. Therefore, the arrangement shown in Fig. 5 was set up to permit attainment of the desired condition. This arrangement was used only for probes without sleeves or caps, inserted from the top to various depths in the fuel. As in the tests in the pot furnace, the small auxiliary probe was inserted in a horizontal, nearly isothermal, plane. The heater was operated continuously at the maximum temperature attainable, so that the bed of crushed coke reached a steady state of temperature distribution.

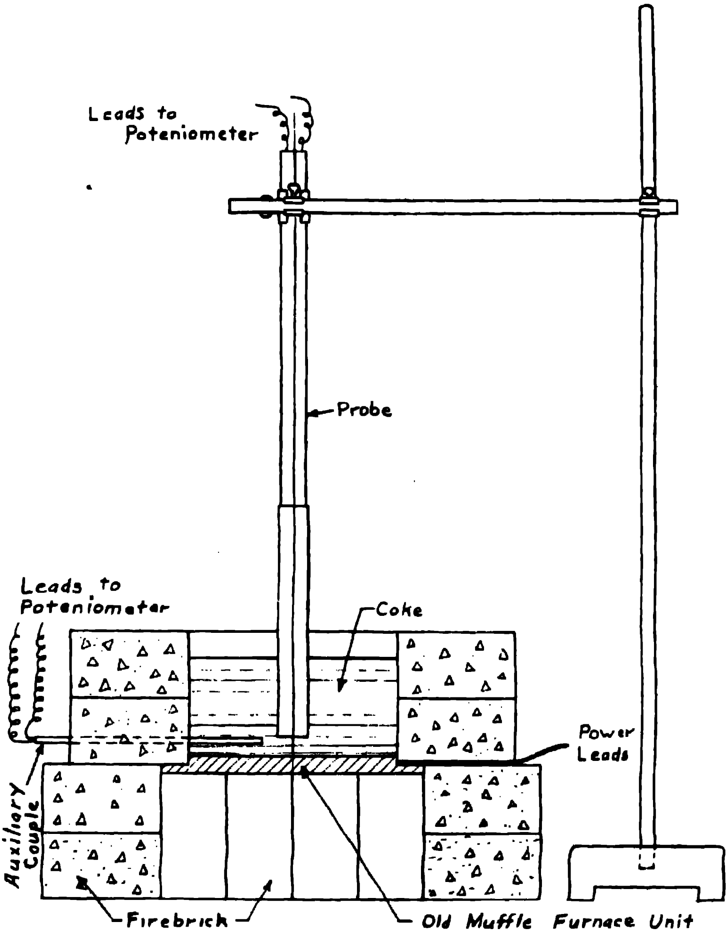

FIG. 5. Electric heating unit for tests of uncapped probes.

Calculations and Results

Since, as shown in Fig. 4, the source temperature in the burning tests in the pot-type furnace was not steady, it was out of the question to attempt a mathematical treatment of the data based on a complete solution of the heat-conduction equation. It might be expected, however, that a simple relation would exist between the rate at which heat was transferred to the probe, represented by the difference in temperature between the source and the probe itself, and the rate at which the temperature of the probe was increasing. If, for instance, there were no conduction along the probe, this relation might be a constant proportion, representing the ratio of the heat transfer coefficient to the thermal capacity of the tip of the probe. Since the data were all in the high-temperature region where radiation was likely

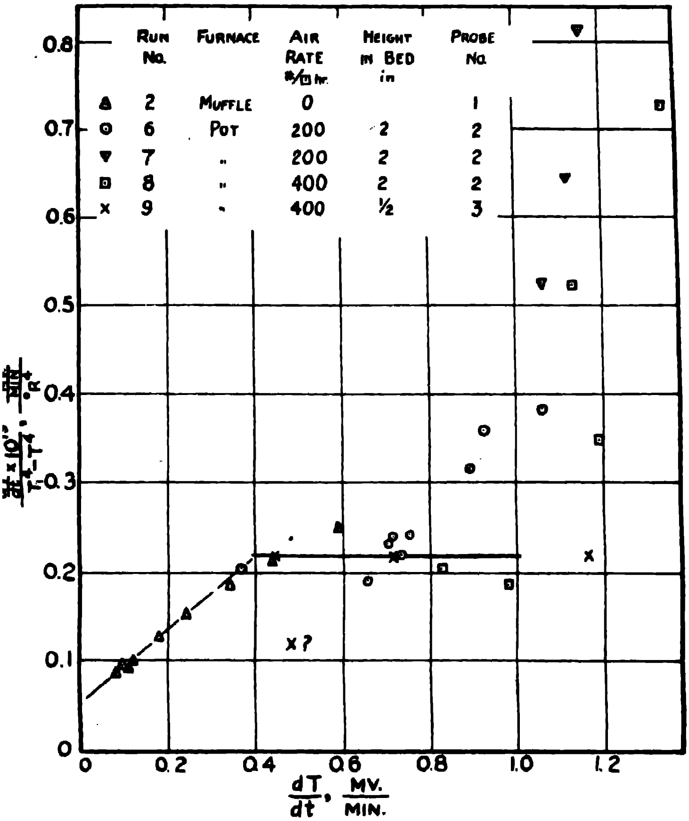

FIG. 6. Relation between rate of temperature rise and temperature difference: capped probes.

T_1 = Temperature of the source (small probe).
T = Temperature indication of large probe.
$\frac{dT}{dt}$ = Time rate of increase of temperature indication of large probe.

to make the dominant contribution to heat transfer, it was logical to use, not the temperature difference itself, but the difference of the fourth powers of the absolute temperatures of the probe and the source. The result of this type of correlation is shown in Fig. 6, in which the ratio of the rate of rise of the temperature indication of the probe $\left(\frac{dT}{dt}\right)$ to the difference between the fourth powers of the absolute temperatures of the small thermocouple and of the probe, $(T_1^4 - T^4)$, is plotted against $\frac{dT}{dt}$. $\frac{dT}{dt}$ is expressed as mv/min, and the temperatures in the difference of their fourth powers as degrees Rankine (°F + 460). Values of $\frac{dT}{dt}$ were obtained by plotting the test results as in Fig. 4 and determining the slopes by the use of the Richards-Roope tangent meter.

It will be observed that a fairly good correlation has been achieved for values of $\frac{dT}{dt}$ less than about 0.8-1.0 mv/min. This applies only to the later part of the temperature history curve. The small values of $\frac{dT}{dt}$ encountered when the probe starts to increase in temperature do not agree with these data. The data indicate an almost constant value of the ratio $\frac{dT}{dt} \Big/ (T_1^4 - T^4)$ over a range of values of $\frac{dT}{dt}$ extending from about 0.4 to about 0.9. Below 0.4, the ratio decreases almost linearly, but cuts the vertical axis. Above $\frac{dT}{dt} = 0.9$, the data scatter over a very wide range, indicating that for very high rates of heat input to the probe other factors than the instantaneous rate of heat transfer help to determine the rate of rise of probe temperature that will be observed. In this region, the ratio $\frac{dT}{dt} \Big/ (T_1^4 - T^4)$ generally increases very rapidly, but the dispersion of the data is too great to permit an estimate of its value. Below $\frac{dT}{dt} = 0.9$, the departures from the curve shown indicate that the curve represents the data to within about 10 per cent.

In the tests on the uncapped probes, the temperature of the source remains constant; consequently the results could be treated by a mathematical analysis. The results of this type of treatment would, however, require rather exact knowledge of the temperature distribution along the probe at the beginning of each series of observations that it is desired to correct. Such knowledge is not usually available, so a correlation similar to that made for the capped probes was attempted as its application requires no other data than those actually observed during the tests. It was found that the use of the same variables as in Fig. 6 produced a different curve for each run; that is, no correlation was obtained. When, however, the quantity $\frac{dT}{dt} \cdot \frac{1}{T_1 - T}$ was used on the ordinate, the curve of Fig. 7 was obtained. The correlation in this case does not cover as wide a range of $\frac{dT}{dt}$ as in the case of the capped probes, and the precision is not as high. It is difficult to account for the appearance of the first powers of the temperatures in the denominator of the quantity given above. The temperatures in these tests were certainly high enough so that radiation would be expected to be the principal agent of heat transfer, just as with the capped probes. The explanation probably lies in the fact that in the uncapped probe the hot junction of the thermocouple is not in intimate contact with any solid material, but both receives heat by radiation from the fuel and itself radiates to the cooler mullite behind it. It can be shown that this may, under certain conditions, lead to a dependence of the temperature of the junction on the difference between the first powers of the bed and of the junction temperatures. Fig. 7 shows a rather large spread of the data about the solid line. The dispersion is, in fact, so great that for values of $\frac{dT}{dt}$ greater than 0.2 mv/min only the limits between which the value of the function $\frac{dT}{dt} \cdot \frac{1}{T_1 - T}$ lies can be given, indicated by the dashed lines extending upward to the right in the figure.

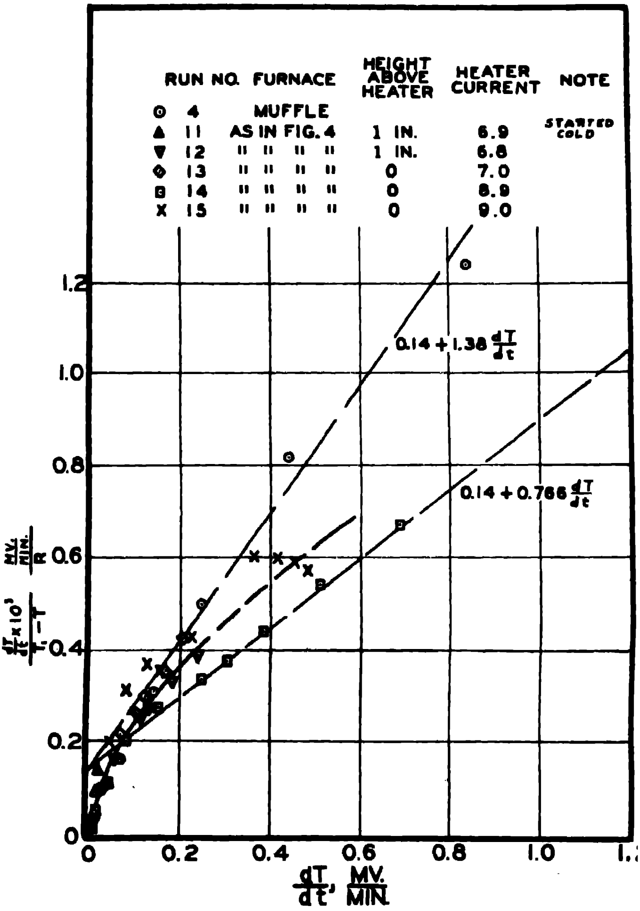

FIG. 7.
Relation between rate of temperature rise and temperature difference: uncapped probes.

Application and Precision

In order to use these results, the test observations are plotted and the values of $\frac{dT}{dt}$ at several times for each point are measured by means of the tangent meter. These values, as well as the actual temperatures at the times of the slope measurements, are recorded as in Table 2. Using the observed value of the slope, the corresponding value of $\frac{dT}{dt} \cdot \frac{1}{T_1^4 - T^4}$ is read from Fig. 6, whence $(T_1^4 - T^4)$ can be calculated. This is added to the value of T^4 corresponding to the observed temperature, giving T_1^4, and hence T_1, the temperature of the source. Several determinations at each point may be made, as indicated in Table 2. The different values of T_1 calculated at each point generally do not differ by more than about 100 °F. Values given in parentheses were obtained by estimation from values of $\frac{dT}{dt}$ greater than 0.9, and so are less precise. For the uncapped probes, a similar procedure is followed as shown in Table 3. In this case, however, the limits between which the true value probably lies when $\frac{dT}{dt}$ is greater than 0.2 is calculated from the two lines of Fig. 7. Except for this the calculation is similar and so will not be described in detail.

Table 2. Correction of Temperature for Probe Lag: Capped Probe.

Run No. 72

Position	Time	T (°F)	$\frac{dT}{dt}$ (mv/min)	$T_1^4 - T^4$	T^4	T_1^4	T_1 (°F)	Recorded Temp. (°F)
				(°F × 10^{-12})				
½	1	930	1.20					
	1½	1000	0.62	26.9	4.55	31.5	1910	1055
1	1½	1315	0.69	29.0	9.92	38.9	2035	1400
	2	1385	0.63	27.0	11.6	38.6	2030	
1½	1½	1710	0.88	28.9	22.2	51.1	2215	
	2	1790	(1.16)	(14.3)	25.6	(39.9)	(2050)	
2	1	2235	1.00	25.0	52.9	77.9	2510	2295
	1½	2280	0.42	20.0	56.4	76.4	2495	

Table 3. Correction of Temperatures for Probe Lag: Uncapped Probe.

Run No. 61A

Position	Time	T (°F)	$\frac{dT}{dt}$ (mv/min)	$\frac{\frac{dT}{dt} \times 10^3}{T_1 - T}$	$T_1 - T$	T_1	Average	$\frac{dT_1}{dt}$	Recorded Temp. (°F)
24½	1	320	1.2	1.70	710	1030	1250	420	570
				1.05	1150	1470			
	1½	470	1.2	1.70	710	1180	1460		
				1.05	1150	1620			
25½	1	1020	1.1	1.67	660	1680	1860	130	1195
				1.97	1015	2035			
	2	1160	0.8	1.24	650	1810	1990		
				0.75	1005	2165			

The precision of the correction to the capped probes is surprisingly high and is limited by the precision of the measurement of $\frac{dT}{dt}$. If this is of the order of ±15 per cent, the precision of the estimate of $(T_1^4 - T^4)$ is of the order of ±25 per cent, since the departures from the curve of Fig. 6 are not greater than ±10 per cent. The error in T is negligible by comparison with this quantity, so that when T^4 is as great as $(T_1^4 - T^4)$, which is usually the case, the error in T_1^4

is not greater than about 12.5 per cent, which leads to an error in T_1 of about 3 per cent. Thus, an estimate of a temperature of 2500 °F (say 3000 °R) will not be in error by more than 90 °F.

The corrections to the indications of the uncapped probes are not so precise, but may be estimated from the spread between the corrections resulting from the use of the two lines in Fig. 7. Over the range of usefulness of the figure, this difference is about 600 °F, and on the assumption that half of the results may be expected to lie in the middle half of this region, the probable error is of the order of 150 °F. While this is a rather large error, it occurs in a region where the temperatures change so rapidly with position that the absolute magnitudes are not of very great importance.

Discussion

It is perhaps not out of order to remark on the probable significance of such measurements as those reported herewith. In a burning fuel bed there are at least two significant temperatures: that of the fuel, and that of the air or gas passing through the bed. These may differ by considerable amounts,[2] and there may be some question about what temperature a probe inserted into the bed actually measures. It is evident that such a probe must measure a temperature somewhere between that of the solid fuel and that of the air or gas passing through the bed. Now, in such cases as those under consideration, the difference between these temperatures decreases at higher levels in the bed and, indeed, may be expected to become negligible at distances greater than 4 to 6 inches above the bottom of the bed, because of the extremely high rates of heat transfer between the solids and gases passing through a porous bed. Hence, the question of the significance of the temperature observed applies mainly to the lower part of the bed. A probe introduced into this region receives its heat mainly by radiation, from a source at a temperature of 2000 °F or above, producing heat transfer at a rate of the order of 60,000 btu/sq ft/hr. The rate of gas flow in this region is unlikely ever to exceed 1000 lbs/sq ft/hr, producing a heat transfer coefficient of about 7.5 btu/sq ft/ °F/hr. Thus, even if the temperature difference between fuel and gas were as great as 500 °F, the difference between the fuel temperature and the indication of the probe would be of the order of only 45 °F.

Conclusion

It is possible to measure the temperatures in a fuel bed with sufficient accuracy for descriptive purposes by the use of refractory probes of large mass carrying thermocouple elements. Even when the probe does not reach the temperature of the bed, the latter may be estimated from the rate of increase of the probe indication when successive readings are taken every half minute for not less than 2½ minutes. The temperatures so observed are probably close to the radiant mean temperatures of a small volume surrounding the end of the probe.

Acknowledgment

The author wishes to acknowledge the coöperation of Mr. P. Nicholls, Supervising Engineer, Fuels Section, Pittsburgh Experiment Station, U. S. Bureau of Mines, in making available the equipment in which the tests on capped probes were carried out. The advice and assistance of Mr. Nicholls and his staff were greatly appreciated.

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Thermocouples for Testing Steam Turbines

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The problem of measuring the temperature of steam flowing in a pipe has been of particular interest to the General Electric Company in making steam turbine performance tests. Such tests are continually and systematically made both to determine how the turbines meet their guarantees and to measure the effectiveness of new designs. Turbine performance is generally expressed as a water rate or steam rate at some specified initial and final steam conditions. The steam rate is usually established by the load-flow method, in which the load, flow, initial temperature and pressure, and back pressure are measured. Recently, however, the use of back-pressure turbines, both for process steam and for superposition in existing plants, has complicated the flow measurement. This development has increased the usefulness of the temperature-drop method, in which the initial and final enthalpies are established by temperature and pressure measurements.

In both methods the initial temperature is fundamental in establishing the initial enthalpy. The accuracy of the temperature measurement is important because the performance is sensitive to the temperature. Roughly speaking, in both condensing and non-condensing turbines, ten degrees error in the initial temperature will result in one per cent error in steam rate when measured by the load-flow method. In non-condensing turbines a 5-degree error in the initial temperature or a 3.75-degree error in the final temperature will result in one per cent error in steam rate when measured by the temperature-drop method. Test results accurate to 0.1 per cent are desirable, and those poorer than 1.0 per cent are of little use.

The temperature-drop method can be used only on turbines with superheated exhausts. The steam rate can be established from the initial and final enthalpies, if the bearing and generator losses, the radiation, and extraneous leakage losses are known, or can be calculated with sufficient accuracy. The temperature-drop method of establishing turbine performance has not in the past been favorably accepted by either the turbine user or manufacturer, because the results obtained on a turbine by this method disagreed with those of the load-flow method. There were two reasons for this: (1) inaccurate steam tables and (2) inaccurate temperature measurements. However, it has recently been shown that satisfactory agreement can be obtained between turbine performance measured by the two methods when modern steam tables, such as for example Keenan and Keyes, "Thermodynamic Properties of Steam," (1936) and thermocouple technic such as described in this paper are used.

The problem of steam temperature measurement may be divided into two parts: (1) the determination of the relation between the steam temperature and the temperature in the thermometer well, or at some other selected point of measurement, and (2) the determination of the true temperature in the thermometer well, or at some other point of measurement.

The first part of the problem has to do with the effect of velocity, heat conduction and radiation, and fluid characteristics on the temperature of the thermometer well. The velocity of a fluid flowing across a smooth well must produce a temperature variation around the well. It also probably produces a temperature in the bottom of the well that is between the static temperature and the total heat temperature. By the static temperature is meant the temperature measured by an instrument moving with the stream, and by the total heat temperature is meant the temperature that would result in the fluid if the velocity were destroyed at the fluid static pressure and with no loss of heat; that is, a temperature which is below full impact temperature by the amount of the Joule-Thomson effect.

In most turbine tests the measured temperature in the thermometer well is assumed to be the static temperature of the steam. At full load the steam velocity is approximately 150 ft/sec, which is a velocity head of ¾ °F. It is estimated that the effect of the velocity is of the order of one velocity head, and that the error introduced by neglecting this effect may be ¾ °F or in extreme cases as much as 1.0 °F.

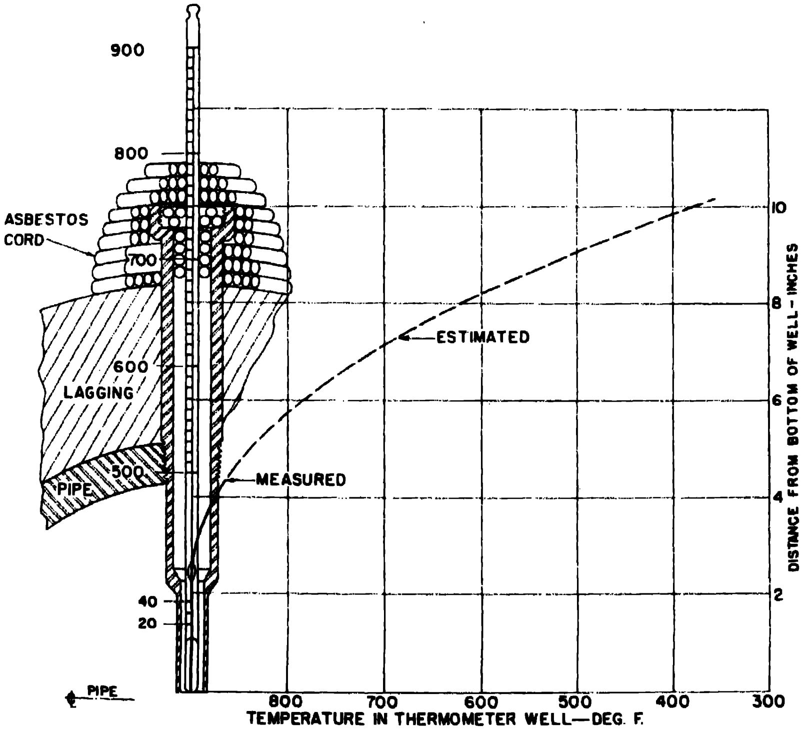

Fig. 1. Temperature distribution along a typical thermometer well.

The effect of heat conduction and radiation is to make the thermometer well appear colder than the stream. Thin-walled wells or fins reduce the effect. When the temperature is constant for an inch or two along the bottom of the well, the heat flow along this portion of the well is close to zero, and therefore the temperature at the bottom is not affected by conduction. The insulation on turbine inlet and exhaust pipes is such that the drop from the stream to the outside pipe-wall is usually less than 10 °F. Therefore, the drop from the stream to the inside pipe-wall temperature is less than this amount. The temperature of the well at the pipe-wall may be colder than the wall itself, as is shown in Fig. 1. However, calculations show that the reduction, by radiation, of the temperature at the bottom of the well below that of the steam is much less than 1 °F unless the mass velocity is very low, say, 10,000 lb per hr per sq ft of cross-section. In turbine tests the mass velocities are usually considerably above this value.

For the purpose of this paper, therefore, the first part of the problem of steam temperature measurement will be dispensed with by the foregoing brief discussion, and it will be assumed that the temperature measured in the bottom of a suitable well is the static steam temperature.

Until about 1930 mercury-in-glass thermometers were used extensively by the General Electric Company for making these measurements in turbine tests. Since that time thermocouples like the ones described here have been used almost exclusively. The purpose of this paper is:

(1) to give the reasons for the choice of thermocouples;
(2) to describe them and their method of construction, calibration and use;
(3) to relate precautions and methods of construction for accurate results;
(4) to illustrate the kind of data obtained with these couples by means of curves showing a comparison of results obtained when a turbine is tested by both the load-flow and temperature-drop methods.

Reasons for Choice of Thermocouples

Thermocouples were used to replace mercury-in-glass thermometers mainly because thermocouples have the following two advantages:

(a) they eliminate the necessity of making stem corrections;
(b) they are usually more easily or conveniently read.

To illustrate how burdensome or inaccurate stem corrections can be, the temperature distribution in a typical thermometer well is shown in Fig. 1. This distribution was measured along the bottom half of the length of the well by means of two thermocouples, one pressed against the bottom of the dry well and the other wedged against the side at various points along the length. The measurements in this case were made to determine the effect of heat conduction along the well and not for the purpose of making a stem correction. They did not, therefore, extend along the complete length of the well and the dotted portion of the curve has been extrapolated. It is probably not far from the true distribution, however, and is sufficiently accurate for our present purpose.

If a typical 900 °F-thermometer were used in this well and the stem correction were made in the customary fashion[1] an error of from 2.5 to 4 °F would result. This result is made apparent by the following considerations. A 900 °F-thermometer might have, as shown in Fig. 1, about 150 °F emergent stem length, 350 °F immersed in the well, and 400 °F contained in the expanded portion of the stem just above the bulb. The usual correction applied to this thermometer would be that calculated for the 150 °F emergent stem, and this would be between 9 and 10 °F. However, since the average temperature of the immersed stem differs from that of the bulb by about 140 °F, an additional correction of 4 °F should be applied for this difference. In addition, if the mercury in the expanded portion of the capillary is colder than the bulb, a further small correction must be added. Thus the proper correction to be applied would be 13 or 14 °F, whereas the ordinary method gives 9 or 10 °F.

If a thermometer of the same length but of a smaller temperature range were used, the error would be less. For example, a thermometer with a range from 750 to 900 °F would require the additional correction to be 2.5 instead of 4 °F. Likewise, a thermometer with a longer range would require a larger correction.

These considerations neglect any effect on the well temperature of the solder or other packing material used with the thermometer. This would generally be such as to reduce the well temperature at the bottom by conduction of the packing material. However, the conclusion can be drawn that, when a thermometer is used, the magnitude of the drop in temperature along the usual well results in either a burdensome procedure to obtain the correct temperature or an appreciable error.

Thermocouples however are especially suited for measuring spot temperatures and can be used to measure the bottom temperature of the well directly. The auxiliary apparatus for reading the voltage of the couple is relatively simple, and once the set-up is made, ten or twelve couples can be read from one station every five minutes. They are more convenient to use than thermometers because the wells are usually not easily accessible.

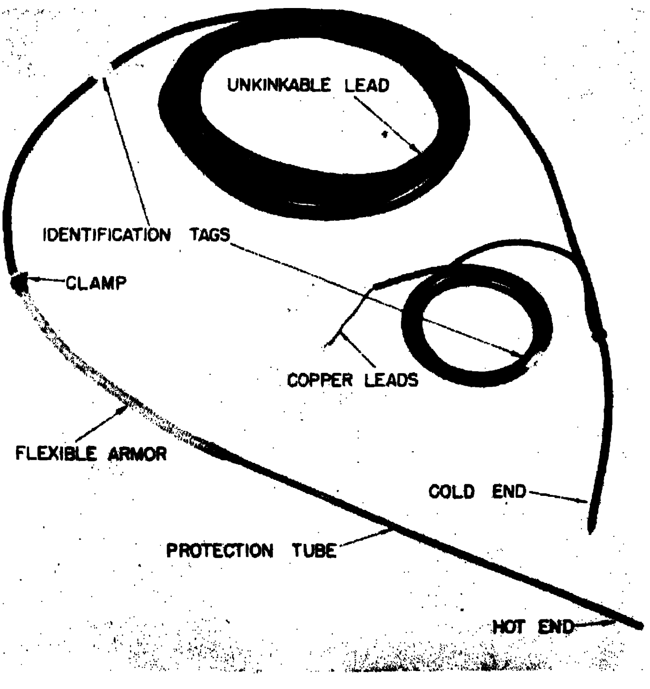

Fig. 2. Thermocouple for testing steam turbines.

For precise measurement in the temperature range required in turbine testing, platinum resistance thermometers are suitable and are generally used in the laboratory. However, these are at present rather fragile instruments to use in turbine tests. Breakage or damage to the instrument would be far more serious than is the case with the thermocouple, where broken hot junctions can easily be made over.

Although the precision obtainable with the resistance thermometer is desirable, it has been thought discreet not to try to use the device for testing turbines at the present time.

Description of the Thermocouple

Fig. 2 is a photograph of one of the thermocouples that are now used by the General Electric Company in testing steam turbines.

The thermocouples are made of Chromel (90 nickel-10 chromium) and Copnic (55 copper-45 nickel) wires, and in lengths of from 40 to 80 feet between the cold and the hot junctions. The wires are continuous between the junctions, so that no terminal block or connection piece is used, as is sometimes the case when separate leads of the same material are connected near the hot end of the couple. The continuous wires prevent errors that might arise from the subjection of the connection points to temperature gradients. Fig. 3 is a cross-section showing the construction.

Two methods of making the hot junction are used: (1) uninsulated; (2) insulated.

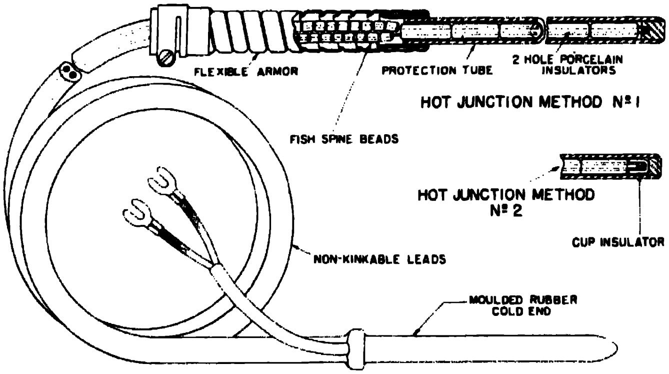

FIG. 3. Method of construction of thermocouple for testing steam turbines.

In the first case the junction is made by welding the wires together, and the bead thus formed is fastened to the steel plug which is finally welded into the end of the protection tube. In the second case the bead is insulated from the protection tube by being inserted in a quartz or soapstone cup which is fitted snugly into the bottom of the closed protection tube. The insulated couples have the advantage that they can be used to measure differential temperatures directly. They have the disadvantage that the thermal contact with the protection tube is less than that of the uninsulated couple. However, calibrations of both types over a range of immersion from 2 to 12 inches indicate that the couple is not affected by the poorer thermal contact even at 2 inches immersion.

From the hot junction the wires are carried in 2-hole porcelain insulators through a $\frac{1}{4}$-in diameter steel protection tube which has $\frac{1}{32}$-inch walls and is from 10 to 16 inches long. The protection tube prevents the wires from being hardened by cold working, and protects the insulation from damage. It is stiff enough for this purpose but thin enough to prevent errors due to heat conduction along the tube even at shallow immersions. Stainless-steel tubes are somewhat stiffer and less conducting than ordinary steel and they are sometimes used. The $\frac{1}{4}$-inch steel tube is connected to a 12-inch length of flexible metal armor by means of a ferrule silver-soldered to the armor and the tube. In the flexible armor the wires are insulated by means of porcelain fish-spine beads for a length of 11 inches. From this point to the cold junction the wires are carried in cotton and rubber insulation in which cord fillers are molded to make the lead round and approximately $\frac{5}{16}$-inch in diameter. A clamp carried on the end of the flexible armor fastens and holds the cord firmly. The armor and the fish-spine beads form a connection between the lead and the stiff part of the couple which carries the pull of the lead and at the same time prevents kinks and sharp bends from forming in the wires. It also serves, in the case of the uninsulated hot-junction type of couple, to prevent strains in the wires inside the steel tube, because of the method of assembly. When the couple is completely assembled, but before the clamp is secured to the lead, the lead is pushed into the armor an amount that will provide $\frac{1}{8}$ to $\frac{1}{4}$ inch of slack in the wires. The clamp is then tightened on the end of the lead. This prevents the protection tube from stretching the wires or from pulling away from the junction when the cold tube is inserted in a hot thermometer well.

The round lead made with a filler is practically unkinkable, and its rubber cover is entirely waterproof. The cover is of tellurium-compounded rubber to make it oil-resistant.

The cold junction is made by soldering to the thermocouple wires two 6-ft copper leads which are insulated in a manner similar to the thermocouple wires to form a cable which is a little less than $\frac{3}{16}$ inch in diameter. The cold junction is carried in a molded rubber covering. This makes a waterproof and unbreakable cold end, and one which has heat conduction properties sufficiently high for the purpose it serves.

Numbered aluminum tags fastened to both the cold and the hot ends serve to identify the individual couples and make it easy to keep track of their locations when a number of them are being connected to one transfer switch.

Method of Calibration and Use

The thermocouples are individually calibrated when they are first made up and also before they are used on each turbine test. They are each calibrated at 6-, 9-, and sometimes also 3- and 12-inch immersions. Usually five or six points are selected in the range from 80 to 1000 °F, and also a check is sometimes made with the hot junction at the ice point.

Fig. 4 shows the thermocouples set up in the apparatus used to make the calibrations. The calibrations are made in the laboratory by direct comparison of the thermocouples with a platinum resistance thermometer in suitable comparators.

The oil bath comparator is used from 200 to 700 °F. It is a cylindrical tank 6 inches in diameter and 24 inches in length, which is heated by a sheath-type heating unit wrapped around the outside. The tank and heating unit are covered with two inches of insulation and enclosed in a sheet-metal case as shown. A cylindrical radiation shield inside the tank forms a central calibrating chamber $4\frac{1}{4}$ inches in diameter. This shield is constructed of two layers of sheet metal separated by a sheet of asbestos paper, and extends to within 3 inches of either end. The high-flashpoint mineral oil used in the bath is circulated by means of a propeller mounted in the bottom of the tank, which gives a circulation up through the space between the shield and the wall and down through the calibrating chamber. Above 400 °F a ventilator, as shown, is used to carry off the vapors. The oil bath has been explored, to determine the temperature distribution, by means of differential thermocouples and found to be uniform to within about 0.2 °F from top to bottom when temperature equilibrium has been obtained.

The copper block comparator is used from 700 to 1200 °F. It consists of a copper cylinder 4 inches in diameter and 22 inches in length, with 12 holes $\frac{3}{8}$ inch in diameter on a 3-inch circle in which to immerse the thermocouples. One hole is provided in the center of this circle and of the copper block for the standard platinum resistance thermometer. A sheath-type heating unit made in the form of a grid is wrapped around the outside of the copper cylinder, and the spaces between the vertical grid elements filled with graphite powder. This is wrapped about with several layers of asbestos paper and 3½ inches of insulation, and the whole is set on a Silocel brick and placed in a 12-inch cylindrical case. This comparator has also been explored by means of differential thermocouples to determine the temperature variation among the several holes and lengthwise of the block. There is no measurable temperature difference from one hole to another at the same vertical elevation or immersion, but there is a gradient in the range of 6- to 12-inch immersion of 0.15 °F per inch. The temperature gradient toward the ends of the block increases to 3 °F per inch at 2 inches immersion in the block.

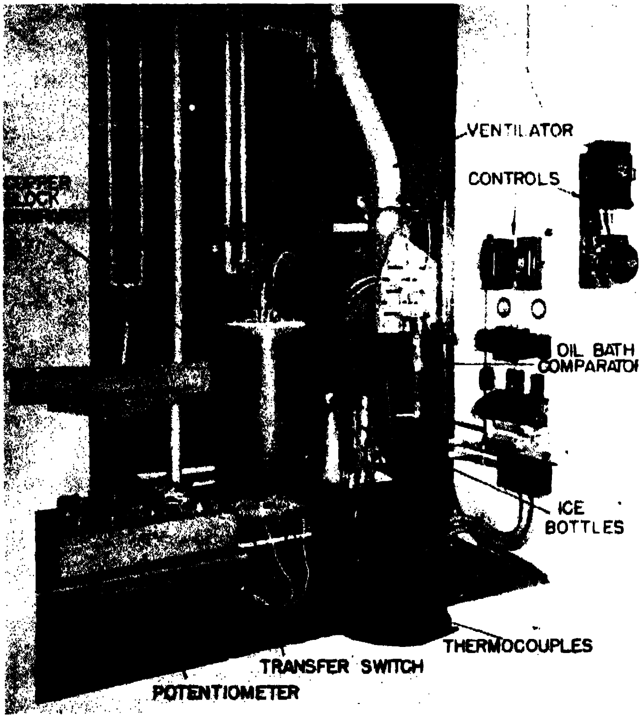

Fig. 4. Thermocouples and apparatus set up for calibration.

To speed up the calibrations in the oil bath, the temperature is determined by means of a mercury-in-glass laboratory standard thermometer for most points. One or two temperatures are read on the platinum resistance thermometer as a check. For the calibrations in the copper block, however, above 700 °F, the platinum resistance thermometer is always read, and for convenience a reference thermocouple is also used. The resistance thermometer and all the thermocouples are installed at the same elevation in the copper block to eliminate corrections for temperature variation along the block.

The platinum resistance thermometer is standardized in the usual way by calibration at the Ice, Steam and Sulfur points. It has a resistance of about 7.4 ohms at 1000 °F which is measured by means of a resistance thermometer bridge to the nearest 0.0001 ohm.

The potential produced by the thermocouple is about 40 millivolts at 1000 °F, and is measured to the nearest microvolt by means of a precision potentiometer and a wall-type galvanometer with lamp stand and scale, as shown in Fig. 4.

For convenience in the use of the couples in testing, the calibrations are expressed in the form of a correction which is obtained by comparing the calibration results of each couple with a reference temperature-millivolt table. The table was computed from equations which represent a smooth curve drawn through the average millivolt temperature characteristic of a group of several of the thermocouples. An example of the corrections thus obtained is shown in Table 1.

Table 1. Calibrations Made on a Thermocouple Used in Four Turbine Tests for Total of Approximately 400 Hours at Temperatures from 150 to 800 °F

Standard Temperat	Immersio	Reference Table (mv)	Date of Calibrations									
			8-11-38		10-7-38		2-1-39		3-13-39		7-26-39	
			Couple (mv)	Correction	Couple (mv)	Correction	Couple (mv)	Correction	Couple (mv)	Correction	Couple (mv)	Correction
32°	6	0	...	...	...	...	...	...	...	...	-.004	+.004
176.7	6	5.00	5.00	.00	...	...	5.00	.00	4.98	+.02	4.99	+.01
	12	...	...	...	...	...	5.00	.00	4.98	+.02	4.99	+.01
308.9	6	10.00	...	...	10.02	-.02	10.02	-.02	9.99	+.01	10.03	-.03
	12	...	...	...	10.03	-.03	10.02	-.02	9.98	+.02	10.03	-.03
432.7	6	15.00	15.03	-.03	15.01	-.01	...	...	...	...	15.02	-.02
	12	...	15.03	-.03	15.03	-.03	...	...	...	...	15.01	-.01
551.8	6	20.00	20.04	-.04	19.99	+.01	20.04	-.04	20.01	-.01	20.02	-.02
	12	...	20.03	-.03	20.03	-.03	20.04	-.04	19.99	+.01	20.00	-.00
668.6	6	25.00	25.08	-.08	25.03	-.03	...	...	...	...	25.06	-.06
	12	...	25.07	-.07	25.07	-.07	...	...	...	...	25.03	-.03
784.0	6	30.00	...	...	30.06	-.06	30.08	-.08	30.12	-.12	30.11	-.11
	12	...	30.08	-.08	30.08	-.08	30.09	-.09	30.11	-.11	30.12	-.12
898.4	6	35.00	...	...	35.09	-.09	...	...	...	...	35.12	-.12
	12	...	35.09	-.09	35.10	-.10	...	...	...	...	35.13	-.13
1012.4	6	40.00	...	...	...	...	40.12	-.12	40.14	-.14	40.14	-.14
	12	...	40.10	-.10	...	...	40.13	-.13	40.16	-.16	40.14	-.14

Note: 0.04 millivolt is equivalent to 1 °F.

Table 1 shows the differences in the calibrations with different immersions and also the changes which take place with use of the couples. The couple which shows the least change in calibration with change in immersion is the most desirable. Differences of less than 1 °F due to immersion are acceptable, but if they are larger than this the hot end of the couple is remade. Between the first and the last calibrations in Table 1 the couple was used for a total of approximately 400 hours at temperatures from 150 to 800 °F.

Thermocouples like the one described in this paper have also been used in the

Table 2. Corrections Obtained from Calibrations at the Lead and Sulfur Points of Thermocouples Used in Six Turbine Tests for a Total of Approximately Sixty Hours. (Data by Mr. J. S. Alford.)

Thermocouple Correction in Millivolts

Thermocouple Number	Before Use		After Two Tests		After Four Tests		After Six Tests	
	At Lead Point	At Sulfur Point	At Lead Point	At Sulfur Point	At Lead Point	At Sulfur Point	At Lead Point	At Sulfur Point
1	+ 0.04	+ 0.05	....	+ 0.05	....	+ 0.05	+ 0.04	+ 0.05
2	+ 0.05	+ 0.01	+ 0.05	+ 0.02	....	+ 0.02	+ 0.05	+ 0.01
3	+ 0.00	- 0.03	- 0.01	- 0.02	....	- 0.02	+ 0.00	- 0.02
4	+ 0.02	+ 0.03	+ 0.02	- 0.03	....	- 0.00	+ 0.03	- 0.01
5	+ 0.03	+ 0.02	+ 0.03	+ 0.02	....	+ 0.02	+ 0.03	+ 0.03
6	+ 0.08	+ 0.04	+ 0.06	+ 0.07	....	+ 0.08	+ 0.07	+ 0.07
7	+ 0.02	- 0.03	+ 0.01	- 0.03	....	- 0.03	- 0.01	- 0.03
8	+ 0.01	- 0.03	- 0.02	- 0.03	....	- 0.04	- 0.02	- 0.04

Note: 0.04 millivolt is equivalent to 1 °F.

General Electric plant at Lynn, Massachusetts. Table 2 shows the corrections obtained from data furnished by Mr. J. S. Alford of the Lynn plant. The couples were used a total of approximately 60 hours between the first and the last calibration and the calibrations were made at the Lead and Sulfur points. Couple 1 was not used on the tests but was kept in the laboratory as a comparison standard and was calibrated each time with the test couples.

In Tables 1 and 2, the corrections do not change more than approximately 1 °F as the immersion is changed and as the couple is used. It may therefore reasonably be expected that temperatures can be measured to the nearest 1 °F, although account is taken of the immersion and the most recent calibration, so that the actual error should be much less, perhaps on the average half this amount.

The couples are used to measure steam and water temperatures both in tests of turbines in owners' plants and in experimental tests at the General Electric plants in Schenectady, New York, and Lynn, Massachusetts. In the outside tests they are used to measure the temperatures at the bottom of thermometer wells installed by the owners in their steam and water pipes. These wells are usually similar to the one shown in Fig. 1. When the couples are installed in vertical wells a drop or two of solder is put into the bottom of the well, and the top of the well is plugged off with asbestos rope and completely covered with magnesia or other insulation. Although the solder is not necessary, it serves to make good thermal contact with the bottom of the well. If only a little is used it does not reduce the temperature by conduction along the well. The asbestos rope serves to prevent cooling of the well by air currents or radiation to the outside, and covering the top of the well reduces the heat loss from it. When used in horizontal wells, the couples are wedged tightly against the bottom of the well with the asbestos rope which plugs off the top of the well.

In the experimental tests at the factory they are used in thermometer wells, and are also mounted through stuffing boxes directly in the steam up to pressures of 200 psi.

When used in the field, the potential of the couples is read by means of a precision potentiometer like the one used for calibration and shown in Fig. 4. The galvanometer used in the field is a portable light-beam type, with a sensitivity of about $\frac{1}{8}$ °F per mm. With this equipment, although it is not as compact as the usual portable potentiometer used in general power-plant testing, the potential can easily be read to the nearest 0.01 millivolt, which with these thermocouples is equivalent to the nearest ¼ °F.

The tests require the use of from 5 to 15 thermocouples. Readings of temperatures are usually taken every five minutes, and since a maximum of about 12 readings can be taken by one observer every 5 minutes, one potentiometer station is usually sufficient.

Normal uniform room temperatures which generally prevail in laboratories are not always found in power plants. To eliminate the effects of rapidly changing ambient conditions, the reference junction or cold end of the thermocouples is maintained in an ice bath. For this purpose wide-mouth Thermos bottles are used, and it is found necessary to replenish them with cracked ice only about twice a day. The copper leads from the cold end are connected to the potentiometer by a transfer switch like the one shown in Fig. 4. The switch is thermoelectrically neutral to copper.

Construction and Precautions for Accurate Results

From the beginning of extensive use of thermocouples for turbine tests by the General Electric Company the goal has been to be able to measure steam temperatures in the field up to 1000 °F with an accuracy of 1 °F or better. The steps toward this desired result which have been taken are:

(1) the use of a reliable platinum resistance thermometer as a calibration standard;

(2) the careful individual calibration of each couple against this standard as described above;

(3) the use of a precision-type potentiometer for measuring the potential of the couples when they are set up in the field, instead of relying on the usual portable instruments;

(4) the use of materials and methods of construction which facilitate the production of thermocouples that are relatively insensitive to depth of immersion and that maintain their calibration over a reasonable period.

During the experience with these couples certain details in the construction have been found necessary or desirable for the production of couples with suitable characteristics. Proper insulation is necessary. It was found, for example, when the couples were made with the wires insulated with felted asbestos, that there were puzzling changes in calibration with time amounting to several degrees F. Brass armor wound over the insulation for its protection against abrasion aggravated the condition. The search for the reason revealed that the wires had an open-circuit voltage between them and also between each wire and the armor, and that the insulation resistance was quite low. It appeared that this type of insulation was hygroscopic and, with the normal room moisture, acted as an electrolyte. Also the length of the couples used probably magnified the effect. The open-circuit voltages were as much as 0.5 volt, with insulation resistances as low as 50,000 ohms. The rubber insulation has entirely eliminated this extraneous voltage and insulation leakage.

Both thorough cleansing before assembly and aging before use are essential. When some of the couples which showed bad immersion corrections were opened they were found to be discolored. They probably contained deposits which contaminated the wires in spots and rendered them inhomogeneous. When these couples were remade with the following cleaning and aging procedure, the immersion corrections practically disappeared:

(a) the insulation is stripped from the ends of the wires and the stripped ends are wiped clean;

(b) the porcelain beads are heated in air to about 1400 °F for a few minutes;

(c) the assembled wires and beads are heated in air about 1200 °F for their entire length for approximately 20 minutes;

(d) the steel tubes are cleaned by heating in a hydrogen atmosphere to about 1400 °F for approximately 20 minutes;

(e) the tubes are slipped on and the ends welded;

(f) the couple is then aged for 4 hours at 1200 °F.

The purpose of heat-treating the wires over the entire beaded length of the couple is to hold the immersion corrections to a minimum. This heat treatment is carried out at 1200 °F, although a temperature of 900 °F would be sufficient to remove the work-hardening strains introduced during the insulating and assembling process. The aging for four hours makes the couple stable. Less time might be sufficient, but at least four hours seems to be ample.

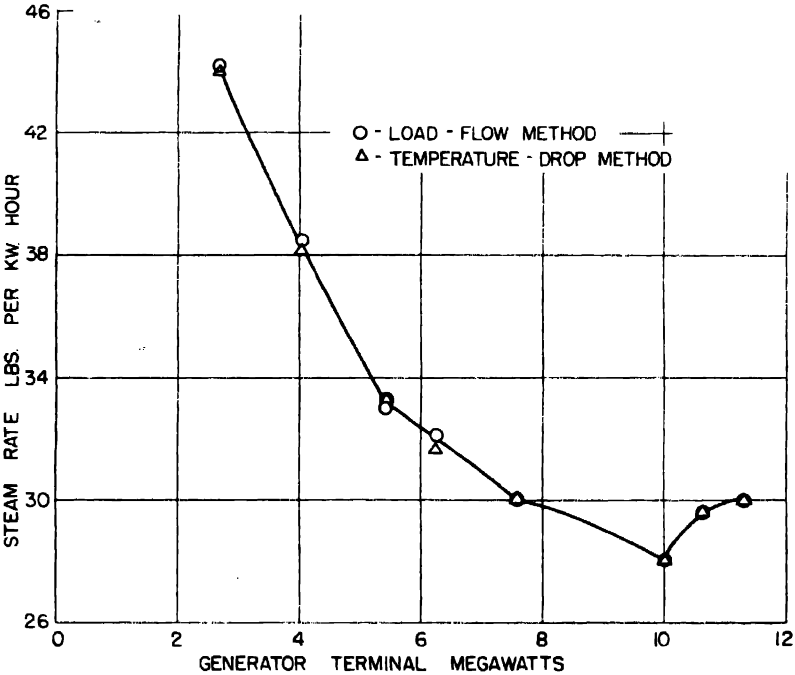

Fig. 5. Comparison of steam rates determined by temperature-drop and load-flow methods.

The following schemes for making hot junctions have been tried in addition to the methods (1) and (2) previously mentioned:

(a) by silver-soldering the wires to the inside end of the small steel plug which is finally welded into the end of the protection tube;

(b) by bringing the two wires through a drilled hole in the steel plug, and by atomic hydrogen-welding of the wires and plug to the end of the protection tube.

Acceptable couples have been produced by all four methods of making the hot junctions, and a number of excellent couples have been made with method (a). However, some very bad couples have also been made with the silver-soldered connection and some fairly bad ones by method (b). Methods (1) and (2), first described, however, have always produced acceptable results; and although the reasons have not been definitely established, these two schemes are recommended on the basis of the evidence up to now.

Example of Data Obtained Using the Couples

Fig. 5 shows a water rate load curve which is the result of using these thermocouples in making a turbine test by both the load-flow and the temperature-drop methods. The circled points are obtained by the former and the triangle points by the latter method. The initial and final enthalpy difference gave the efficiency of the turbine exclusive of bearing and generator losses and extraneous packing leakage and radiation loss. To obtain the water rate the calculated values of these losses were used. The bearing and generator losses vary from 3 per cent at 11,000 kw to 11 per cent at 2700 kw. The combined extraneous leakage and radiation loss varies from 1 per cent at 2700 kw to ¼ per cent at 11,000 kw.

Table 3. Location and Dimensions of Thermometer Wells Used in Turbine Test, Results of Which Are Shown in Fig. 5 and Table 4.

Temperature Measured	Approximate Location	Type of Well	Depth of Well (inches)	Approx. Length of Well Inside of Pipe (inches)	Pipe Size (inches)
Throttle	15 ft ahead of throttle	Vertical	9¼	3½	12
Throttle check	1 ft ahead of throttle	Horizontal	12	6	12
Exhaust	15 ft from turbine flange	Vertical	10⅜	5	18
Exhaust check	30 ft from turbine flange	Horizontal	8¼	4	18

Two thermocouples were installed in both the inlet and the exhaust pipes during the tests. The thermocouples were installed in separate wells, the location and approximate dimension of which are shown in Table 3. A sample of the temperatures indicated by these couples which is typical of results obtained in the field is shown in Table 4.

Table 4. Comparison of Inlet and Exhaust Temperatures Measured During a Turbine Test. The Steam Rate Obtained on the Turbines is Shown in Fig. 5.

Turbine Flow (lbs/hr)	Throttle Temp. (°F)	Throttle Check Temp. (°F)	Exhaust Temp. (°F)	Exhaust Check Temp. (°F)
124200	764.3	766.0	559.7	560.8
158000	810.7	810.4	576.1	577.0
202700	841.1	841.1	580.4	581.0
225600	862.8	862.6	588.9	589.3
286700	877.1	876.6	584.9	585.2
282800	871.1	870.7	571.1	571.7
310200	871.6	871.4	593.0	593.7
335600	873.0	872.7	594.1	593.9

In all but the smallest flow point, the two throttle temperatures agree within ½ °F or less and the two exhaust temperatures agree within 1 °F or less. The increasing difference shown between the two throttle temperatures as the flow decreases might be taken to indicate that the shallow well is reading below the steam temperature at the low flows. The increasing difference shown between the two exhaust temperatures is probably also due to conduction effects.

With such agreement as shown by Fig. 5 possible, the importance of the temperature-drop method of testing is very much increased. The method is of increasing usefulness because the increased complication of power-plant piping circuits, brought about by the advance in the art of power generation, has made the testing of turbines by the load-flow method more difficult and complicated. In some superposed turbines which discharge into large low-pressure systems, and which are fed with several boilers, the measurement of flow by means of weigh tanks or nozzles especially installed for the tests is entirely too complicated and expensive. The station-operating meters must, therefore, he relied on for flow measurements; and although these meters serve the intended purpose very well, the precautions necessary to get results from them to 1 per cent accuracy or better are not always possible. The temperature-drop method is always easy to apply and it thus becomes a very useful tool to insure accuracy in performance measurements.

Discussion

J. S. Alford, Lynn, Mass.: The excellent agreement shown by Messrs. Buckland and Stack between steam turbine efficiencies, as obtained from measured steam flow and turbine output, and temperature-drop efficiency is the result of refined thermocouple construction and calibration, and a great amount of experience in accurate steam turbine testing. Deserving of particular praise is the modern accurate research work on the thermodynamic properties of steam, which makes temperature-drop efficiency tests possible.

Unfortunately, not all non-condensing steam turbines can be tested by the temperature-drop method. Aside from the obvious requirement that the steam leaving the exhaust must be superheated, there must be considered the important relation of turbine heat loss (which includes radiation, conduction, and convection heat losses) to the turbine output. What is actually determined by the temperature-drop turbine test is the sum of the equivalent work output, plus heat loss per unit mass of steam. Therefore, the equivalent work output can be found only when the heat loss is negligible, or is accurately known if of appreciable relative magnitude.

The uncertainty in the heat loss limits the applicability of temperature-drop tests to rather large non-condensing turbines. The following table gives an estimate of the uncertainty in temperature-drop test turbine efficiency due to uncertainty in the heat loss, for the medium-sized machines:

Turbine Rating (Kilowatt)	7500	5000	3000	2000	1000	500
Estimated Uncertainty in Temperature-drop Test Efficiency at Full Rated Load, Due to Uncertainty in Heat Loss (%)	0.3	0.4	0.6	0.8	1.3	2.0

To obtain the actual steam rate of a turbo-generator set from temperature-drop tests, the mechanical, generator, and excitation losses must be accurately known, as the sum of these items must be subtracted from the temperature-drop test wheel output. The ratio of the sum of these losses to the generator output also increases with decreasing turbine size. Although these losses are known much more accurately than the heat loss referred to above, they must nevertheless be assumed, unless separate tests of these losses have been made on the particular machine. Therefore, the purchaser of a turbo-generator set, who is generally more interested in the overall unit efficiency than in the turbine's internal efficiency, may object to the temperature-drop tests, particularly on smaller turbines.

To obtain the overall turbine efficiency from temperature-drop tests, measurement of the high-pressure packing leakage steam flow must also be made.

The quantity which must be known accurately for determining turbine efficiencies from temperature-drop tests is the impact enthalpy of the steam in the turbine inlet and exhaust pipes, for it is the difference of these two quantities which equals the work output (plus heat loss) per unit mass of steam. But, since the steam is flowing with appreciable velocity past the stationary thermocouple, which is generally inside a circular well, the question always arises as to the relation of the "indicated" temperature to the temperature that should be used, along with the measured static pressure, in entering the steam tables to obtain the impact enthalpy. The practical answer to this point is to not attempt accurate steam temperature measurements where velocities are high. Tests have shown that if the steam velocity is not greater than 140 ft per second, the temperature indicated by a circular finned well inserted in a straight run of circular pipe will not be more than 1 °F below the impact temperature.

Reply

Mr. Alford's estimate of the uncertainties due to the radiation and convection losses is about correct.

Concerning the packing leakage loss, however, the following should be added: In almost all modern non-condensing turbines the high-pressure packing is bled to the exhaust of the turbine in such a way that the leakage to atmosphere accounts for a small fraction of 1 per cent of the output. When the temperature is measured sufficiently far downstream to allow the leakage which is bled to the exhaust to mix thoroughly with the main flow, then the performance indicated by this temperature reading properly accounts for all of the packing leakage loss, except that which leaks to atmosphere and which is called in the paper extraneous leakage.

The wake behind an obstruction in the stream does not disappear completely until the steam has traveled about 8 diameters of the obstruction downstream. The work done on the stream by the obstruction, therefore, is not completely returned to the stream in the form of heat until this distance has been traversed. Thus, in general, a transverse tube might be expected to be colder than what is defined in the paper as the "total heat temperature," which temperature, of course, is practically always equal to or less than the impact temperature.

The results of a somewhat incomplete investigation by the author show that the temperature in the bottom of a finned thermometer well set approximately across the stream, even at high velocities, reads very close to the total heat temperature. The same temperature seems also to be indicated on the inside pipe wall.

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1. See A.S.M.E. Power Test Codes, Series 1929, Instruments and Apparatus, Part 3, Chapter 6, Par. 18.

Temperature Measurements in the Molding of Plastics

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A large proportion of organic plastic materials produced in this country today are made available as pressure-molded articles fulfilling a wide variety of requirements. While cold molding followed by a baking period is practiced by a few molders, most organic plastics are molded under heat and pressure. The technic of molding these materials is a specialized art, in which much reliance has been placed upon the operator's experience, uniformity of quality in the molding material, and the dependability of heat and pressure sources. Recent trends in the plastic-molding industry indicate a shifting of some of the responsibilities of the operators to automatic control devices, in order to reduce rejections due to errors of judgment. This has meant, among other things, more elaborate temperature measurements and controls than have hitherto been employed. Noteworthy examples of this trend have appeared in recent models of fully automatic injection- and compression-molding equipment.

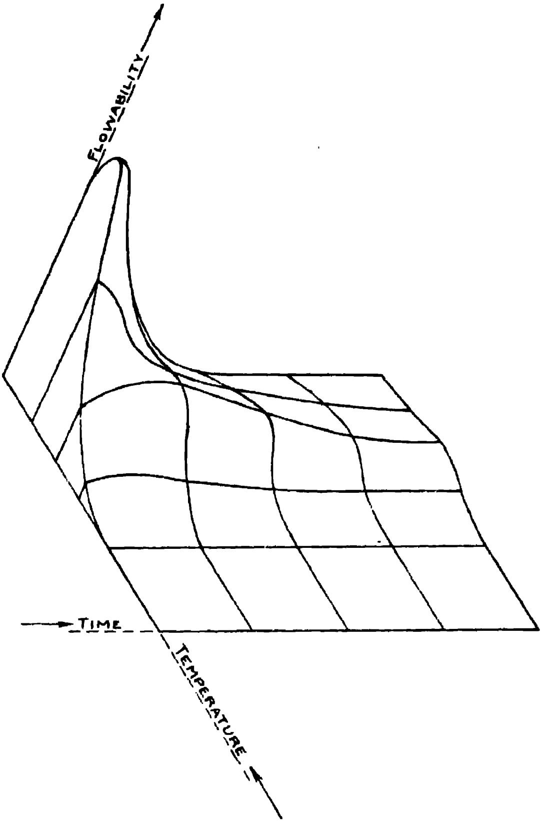

Fig. 1.
General flow characteristics of thermosetting materials.

Though all organic "plastic molding" compositions flow under heat and pressure, some of them become hard and infusible, whereas others remain plastic indefinitely until the molding temperature decomposes or burns them. The thermosetting resins, as typified by molded phenolic and urea plastics, possess flow characteristics as illustrated in Fig. 1. The behavior of materials at different molding temperatures is represented by an arbitrarily chosen flowability ordinate, which may represent flow characteristics, such as the extent of flow under pressure. Thermosetting compounds rapidly lose their flow properties after exposure to high temperatures above 220 °F for any length of time, and hence may be said to be more critical as regards temperature than are thermoplastic materials. In contradistinction to the thermosetting resins are the thermoplastic materials, such as the cellulose plastics, methyl methacrylate, polyvinyl resins, and polystyrene, which flow as long as heat and pressure are applied. Their characteristics are qualitatively illustrated in Fig. 2, showing relatively little loss of flowability with time. However, while these materials flow longer at molding temperatures, the molds must be cooled below the temperature distortion point of the material, so that the molded pieces will not be deformed as they are pushed from the cavities by the ejector pins. On the other hand, many of the thermosetting materials can be ejected successfully while they are relatively hot, because of their higher distortion temperatures.

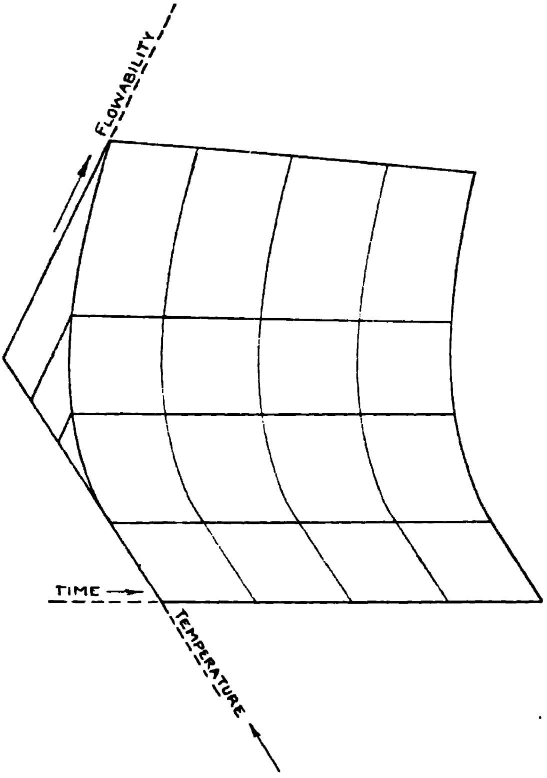

FIG. 2.

General flow characteristics of thermoplastic materials.

A more favorable thermal condition exists in injection molding, where the hot, highly thermoplastic material is forced into a cold die under high pressures. Under these circumstances the cooling period is a matter of only a few seconds, as the molding material rapidly gives up its heat to the large, cool mass of metal in the mold. These problems are discussed at length in a recent text.[1]

Compression Molding

Heat Transfer. From the standpoint of mathematical analysis of the heat-transfer problems, the ramifications of compression molding and the many sizes and shapes in which molds appear are too multifold to attempt to formulate a general expression. Consequently, among the great majority of molders there is much cutting and trying until the optimum pressure and temperature are ascertained for a given design. However, there are fundamental factors which influence heat transfer in compression molding that are studied in an effort to determine the best molding conditions. These considerations are tabulated and discussed below:

(a) Difference between the temperature of the mold and the temperature of the material at the time it is introduced into the mold. It is a well-known fact that preheating the molding material to reduce the temperature gradients at the mold surfaces permits the material to flow sooner, reducing the mold-closing time.

(b) Thermal properties of the molding material. While there are not very great differences in specific heat among the more common molding compounds, there are many factors which influence their thermal conductivities, such as the "bulk factor" of the material, whether it is preformed or not, and resistance to the compressive forces exerted by the mold when it is closed. If the material is relatively soft it will be spread against the hot surfaces of the mold more readily and be brought up to molding temperature sooner than a harder material.

(c) Ratio of total surface area of molded article to its volume. An important consideration after flow has commenced is the ratio of the total surface area to the volume, for there is a tendency toward more rapid setting and shorter curing, the greater this ratio. On the other hand, where very large areas are involved, particularly where they lie in a plane parallel to the line of molding pressure, the distribution and flow of molding materials to these surfaces are often serious problems. They are usually solved by employing a material with a long setting time, which may offset any time savings in the entire molding cycle.

Heat Losses. Heat is lost by conduction from the molds and platen to the large mass of the molding machine making up the table, ram, frame, etc., of the press. It is frequently necessary to make some correction or allowance in the heat supply for the upper half of the mold which tends to be hotter due to convection currents from the lower portion. Radiation losses to the atmosphere, and other parts of the press are quite high; in fact, only a small percentage of the total heat supplied reaches the molding material. The nature of the molding operations has some bearing upon the heat losses. For example, when hand molds are employed and heat transferred from a steam platen, the losses are quite high, as the molds are carried from the steam platen to the unloading fixture. Permanent mounting of molds and the direct steam heating of semi-automatic molding have many advantages, as the heat losses will be constant and the molding cycle and molding temperature may be regulated to give the best results. There is an increasing tendency toward more accurate cycle control in compression molding where mold-closing time, breathing, curing, and ejection are automatically provided in the design of the machine, requiring an operator merely to remove the molded pieces and load the cavities with material. The success of these operations is dependent to a large measure upon the maintenance of the correct molding temperature.

Measurements. While very dependable temperatures with constant-pressure, saturated steam heat can be obtained, the ramifications of molds make it impossible to expect uniform temperatures of their surfaces. Theoretically, the temperature gradient between a molding surface and the steam ports depends upon the distance from the steam ports, heat capacity and thermal conductivity of the mold steel, location of the surface with respect to the rest of the mold cavity, and radiation and convection losses. This temperature gradient may be as much as 20 or 25 °F, and for this reason molders feel that the only positive test of whether the correct molding temperature has been attained is to mold pieces under production conditions, after the heat losses have reached a steady rate. If the articles are molded satisfactorily within a reasonable molding cycle, it is very likely that the mold surfaces are within the allowable temperature range.

However, molders keep on hand portable surface pyrometers for checking the temperature of molding surfaces. This is quite important for materials such as urea plastics which have a limited molding range, and which lose their attractive appearance if molded above or below the prescribed limits. Some of the compression-molding temperature ranges recommended by manufacturers of the materials are given in Table 1.

Table 1.

Molding Material	Recomn.ended Compression Molding Temperature Range (°F)
Urea-Alpha Cellulose Filler, Standard Medium Grade	300–320
Cellulose Acetate, Grade MS	285–305
Phenol-formaldehyde-wood flour filler	280–360
Methyl Methacrylate, Grade M	320–350
Polystyrene	240–350
Polyvinyl Chloride-Acetate	250–300

For the forming or molding of large bearings or gears from laminated phenolics, fabric reinforced, some manufacturers have equipped their standard molds with recording thermometers to obtain a record of the varying temperature conditions. Temperatures are maintained on the mold surfaces in the neighborhood of 345 °F for a period of about one-half hour. The recording instruments are particularly valuable for long molding cycles, because the operator may devote his time to several presses, making periodic checks of the time and the temperature on the recording chart. On the other hand, when very much shorter molding cycles are in progress and multiple-cavity molds are employed, there may be some question as to the efficacy of a continuous temperature-recording instrument, which may give a correct reading for one mold, but not necessarily the others. A useful guide to the average temperature throughout all the molds is the steam-pressure gage at the steam inlet to the mold structure.

Preheating. Of increasing importance in the molding of thermosetting compounds is the practice of preheating materials before they are placed in the molds. In the past, this practice has been abused in the absence of proper temperature control, with the result that the benefits normally accruing from preheating are lost. For example, many operators have been in the habit of placing tablets or "preforms" of the molding material upon platens which were far in excess of the temperature required for preheating. It has been shown[2] that as preheating temperatures for phenolics exceed 200 to 210 °F, the time during which the molding materials should be kept at those temperatures becomes very critical, with the result that the material may lose some of its desirable flowability due to an advanced stage of polymerization brought on by the excessive heat. On the other hand, when the materials are maintained at temperatures below 200 °F through the use of proper temperature control, in a properly designed preheating chamber with no "hot-spots," the benefits of preheating are realized. When preheating has been properly conducted, the mold-closing time is reduced because the material is brought up to molding temperature sooner, and the previous removal of moisture and volatile matter from the molding powder results in a reduced curing time and an improvement in physical properties. In some of the more recent designs of preheating units, metallic containers for measured amounts of molding powder required for one mold cavity are tumbled about so that a more uniform heat distribution will be obtained. Otherwise, if the container is stationary, there will be a temperature gradient from the powder nearest the walls, which are at the preheating temperature, to the center of the mass.

It may also be brought out in the discussion of preheating that similar methods are practiced for blanks of thermoplastic materials that are to be "swaged" to a given shape in a forming die. In such molding operations, the flow of material is very limited. Preheating is necessary only to raise the temperature of the material above its heat-distortion point, allowing it to form readily when struck a sharp blow in the die. The chilling action of the cool mass of metal will cause the material to hold its shape.

Fully Automatic Compression Molding. Much time and study have been given to the development of fully automatic compression molding of thermosetting materials, wherein automatic control of molding temperature is an important requirement of the cycle of operations. When using electrically heated platens, sensitive temperature-indicating controls are employed for each platen, keeping the temperature accurate within a few degrees. The thermal-responsive elements are employed to operate relays in the press, which deliver full electrical power to the heating cartridges.

Injection Molding

Heat Transfer. Injection molding has been designed primarily for the molding of thermoplastic materials, which are forced through a nozzle and suitable gates into molds that are tightly closed. Practically all the recently developed injection molding machines are designed for fully automatic operation, and close attention has been given to the heat-transfer problems incurred therein. Unlike compression molding, where the material is plasticized by the heat flowing from the molding surfaces, the material in injection molding must be fed into a plasticizing chamber where it is heated to molding temperature before injection. The high temperatures employed will not permit the molding material to remain in this state for too long a period; otherwise it will be burned or decomposed. The success of the process depends upon close cycle control, wherein a constant output rate must be maintained for a given heat input to the plasticizing chamber.

In analyzing heat-transfer problems in injection molding, one must consider the flow of material from the time it leaves the hopper feed to its entrance into the injection mold cavities. It is the practice to chill the loading end of the plasticizing chamber and the bushing for guiding the injection plunger with cool water. The cooling water is usually circulated by the same pump that circulates cooling water to the molds. Following the loading entrance is the main portion of the plasticizing chamber, where the materials are brought up to the molding temperature and forced through a nozzle into the mold by the injection plunger. In order to improve upon the heat transfer from the walls of the plasticizing cylinder to the material, a spreader (sometimes called "pineapple" or "torpedo"), is employed to reduce the cross-section of the material to a very thin layer where it passes the main heating surface. In this manner the material is brought rapidly up to the molding temperature as it flows and makes intimate contact with the heating surfaces. In all the recently designed injection molding machines, particular efforts are made to control this temperature accurately by means of suitable temperature-responsible elements, one usually being mounted in the wall of the plasticizing cylinder, as close to the material as mechanically feasible, and the other close to the injection nozzle. Heating units in both locations are controlled individually by their respective thermal-responsive elements. How close the molding material attains the temperature indicated by the instrument has been open to some question, because of the thermal properties of the material being heated. The plastics are relatively good heat insulators, and a considerable temperature gradient is bound to exist, though if the material is thinned out by the spreader much better results can be obtained. Extension of the thermal-responsive elements away from the walls into more intimate contact with the molding material has its drawbacks for mechanical reasons, *viz.*, by offering an obstruction to the flow of the material through the plasticizing chamber. However, custom molders know from experience that for certain temperatures as indicated on their thermometers, they are able to mold certain pieces satisfactorily, and hence guide themselves on a comparative basis.

It is probable that considerable time is required for the concentric spreader within the plasticizing cylinder to attain temperatures approaching those of the walls. This is true for injection molding machines that rely upon external heating units in the form of resistance coils, or indirect electrical heat through a circulating hot-oil medium. The heat must flow from the walls of the plasticizing chamber to the spreader by conduction through the material. Some measure of success, however, has been attained by one manufacturer of injection molding machines who employs an electromagnetic heating method, utilizing the eddy currents in the steel walls of the plasticizing chamber and spreader, set up by a strong alternating field, to build up the molding temperature.

Flow through Nozzle. To improve the conditions of plastic flow and make up for loss of heat at the nozzle adaptor, the injection nozzle is usually provided with additional heating coils whose temperatures are automatically controlled. Temperature-responsive elements are placed as close to the material as feasible. The operations of the injection-molding machine are timed so that the contact of the hot nozzle with the relatively cool molds is as short as possible, so as to avoid chilling the nozzle and hence freezing a long stem of molding material which may have to be cleared out of the way before another shot is made.

Material as it Enters the Mold. If a discrepancy exists between the temperature readings of the instruments outside the plasticizing cylinder and the molding material, what then is the temperature of the material as it enters and flows through the mold, where the heat is very rapidly transferred to the relatively large, cool mass of the mold surfaces? Inasmuch as only a few seconds are required to chill the material in the molds to a low enough temperature to permit ejection of the molded articles, from a practical standpoint the temperature of the material in the mold can only be expressed as a gradient. A rough integration would correspond to the rate of chilling and the ejection temperature of the piece. The writer has been able to evaluate the nature of this temperature gradient in some injection molds that employ large metal inserts about which the molding material flows. This is accomplished by coating the metal insert with thin layers of materials that will soften at the temperatures attained. The layers should be thin enough so that the mass is small compared with the mass of the molding material. In some instances a hard sealing wax has been satisfactory, the coating disappearing entirely in the vicinity of the gate, where the molding material would be expected to be the hottest, and gradually appearing the farther away the material is from the gate entrance, where the material is cooler. Flow patterns of the molding material may also be studied in this coating over the insert. In one case under examination, approximately 1/12th of the mold surfaces attained for a very short period a temperature sufficient to flow away the wax coating (melting point 217 °F), while over the rest of the surfaces the wax did not melt. This indicates the rapid cooling along the nozzle adaptor and the gates. At the time of injection the temperature of the material in the plasticizing chamber was 400 °F, according to an indicating instrument.

Consequently, from a temperature-measurement viewpoint, injection molding presents many problems due to the complex nature of the heat transfer from the moment the material enters the plasticizing chamber to the moment it is ejected as a molded article. While the attainment of certain temperatures in the plasticizing cylinder has been shown to be highly important to the success of fully automatic operation, the molder must not lose sight of the significance of the temperatures of the material in the nozzle and in the molds themselves, for good molding is dependent upon favorable behavior of the material in these regions.

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The Control of Temperature in Massive Concrete Structures

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I. General Nature of the Problem

The problems involved in controlling the temperature of a large mass of concrete present some features which are unique in many respects. The temperature change which is most significant is that due to generation of heat within the material itself, and that factor introduces a condition which was given only scant consideration in the classical investigations of the mathematics of heat transfer. Furthermore, the usual purpose of the temperature control is to reduce inherent stresses, and a mere reduction of the maximum temperature, or an acceleration of the rate of cooling, does not always present the most appropriate solution to the stress problem. A more effective or more economical solution may sometimes result from the control of the rate of temperature change or control of the distribution of temperature.

The problem is further complicated by the fact that massive concrete structures are built up gradually, so that the dimensions of the structure may change during the period being considered. Adjoining or successive sections, or lifts, may be cast at different temperatures, may contain different amounts of cement, and at a given time may be generating heat at different rates. This method of construction facilitates the control of temperature, but it has introduced rather formidable difficulties in understanding the nature of the temperature changes which require control.

The most obvious result of unfavorable temperature conditions in a concrete structure is the development of cracks which detract from the appearance, destroy continuity, and thus alter the conditions of stress and stability, and which may reduce the life of the structure by providing focal points for erosion or disintegration. Under the most adverse conditions, a temperature drop of 20 °F may be sufficient to crack concrete; so it is apparent that with present materials the complete elimination of temperature cracking in all types of concrete structures is scarcely possible. However, experience has shown that careful control of materials and construction methods may result in pronounced reduction in the amount of cracking. Temperature stresses which do not produce cracks are usually considered as unimportant, but as knowledge of these inherent stresses is acquired, their control may permit refinements in design which will result in safer or more economical structures. The deformations which result from temperature changes are sometimes of importance, particularly when parts of large machines, such as hydraulic turbines, are embedded in massive concrete sections.

The proper control of temperature in a large concrete structure is likely to be an expensive undertaking, so haphazard methods of doubtful value cannot be justified. Present practices, and new procedures which are continually developing, have resulted from the study of temperature measurements in a large number of structures and from theoretical investigations of the mathematical and physical relationships which determine the distribution of temperature under the complex conditions encountered in construction. To the measurements which have been made on service structures must be credited the recognition of the importance of temperature control and the incentive for theoretical studies; but to the latter must be ascribed the understanding of the phenomena involved and the definite recommendations which have resulted in improved methods of construction. The physical problem which is usually involved may be stated briefly thus:

> A layer of material of given depth (the first lift of concrete) which is generating heat is placed on the surface of a semi-infinite solid (the foundation) which is not generating heat. The thermal properties of the two, and also their initial temperatures, may or may not be the same. The dimensions of the concrete layer may be such that for certain purposes it may be considered of infinite extent. If the boundaries must be considered, it may be required to account for the effect of the forms, which will be removed after a specified time, or for the effect of adjoining sections of concrete. After the lapse of a certain time, during which the ambient temperature may be changing, another layer is placed on top of or adjacent to the first one. This process is repeated until completion of the structure. In some cases, artificial cooling methods may be included for the removal of heat from the interior. The requirement is to determine for any time the temperature at any point, or the distribution of temperature along any line.

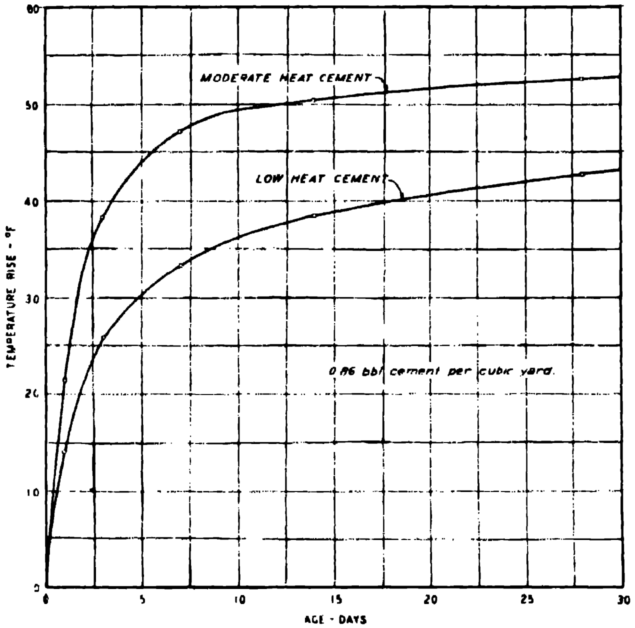
The problem has been stated in a rather comprehensive manner, for all the factors mentioned may require consideration in selecting the proper control procedure. Fortunately, however, it is usually feasible to study the various factors individually. It is in this respect that computation methods have a certain advantage over measurements, for the separation of the variables, solely on the basis of observed temperatures, has generally been found impossible. On the other hand, the entire problem, involving all the variables, is so very complex that actual measurements provide the only feasible present solution. When a complete temperature record is required, as when temperatures are to be correlated with measured stresses or deformations, or with observed cracking, then temperature measurements are required. When the effect of an individual factor is in question, as the effect of varying the thickness of the lifts, then computation methods serve better. Needless to say, such computations should be based on laboratory determinations of the properties of the particular materials involved.

II. Discussion of the Variables

The statement of the physical problem, as given above, suggests numerous variables which may be controlled in order to improve temperature conditions. The ones which are usually considered are enumerated below:

(1) Heat Generation. Portland cement is a material of complex composition. Its exact chemical nature is not readily determinate, but it is usually considered as consisting principally of four major compounds: dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetra-calcium aluminoferrite. Of these, the tricalcium silicate and the tricalcium aluminate are the principal contributors to heat generation. Thus, the first step in temperature control is to control the composition of the cement. This factor is complicated by the fact that heat generation and the early development of strength are closely connected, so that complete control by this method is not feasible. In the so-called low-heat cements, the percentages of the two tricalcium compounds are limited, resulting in a somewhat lower total amount of heat generation and a decidedly lower early rate of heat generation. This lower early rate is of particular importance in controlling temperatures, especially when low-heat cement is used in conjunction with artificial cooling by embedded piping. The adiabatic temperature rise of a typical concrete containing 0.86 barrel of cement per cubic yard of concrete is shown in Fig. 1.

The amount of heat generated per unit of concrete depends directly upon the cement content, so variation of this factor presents another possibility for temperature control. It may be presumed that for reasons of economy the cement content will be fixed at the lowest which will produce concrete of the required strength, durability, and impermeability. However, a nice problem is sometimes presented in deciding whether the lower strength which results from a low cement content is more or less desirable than the temperature cracks which may accompany a higher content.



ADIABATIC TEMPERATURE RISE OF CONCRETE

FIG. 1.

(2) Placing Temperature. If the concrete were placed at a temperature sufficiently low that the heat generation would bring it up to the ambient temperature, then the conditions arising from temperature differentials would be largely eliminated. Procedures which approach this condition have frequently been given consideration, but up to the present time have not been used in any important work.

A certain amount of precooling of the materials is generally advantageous and is entirely feasible. Cooling of the mixing water alone may suffice to lower the placing temperature by 5 to 10 °F. The advantage gained by precooling is, of course, gradually dissipated, and since maximum temperatures in some cases may be reached at a month or more after casting, the effect on the maximum may be considerably reduced.

(3) Dimensions of the Structure. The overall dimensions of the structure will, of course, be fixed by considerations other than those of temperature; but in detailing the size of the construction units, temperature considerations may be involved. In certain cases, gaps or slots have been left between the units in order to accelerate the rate of cooling. In other cases, the specifications have required that adjoining units be cast as nearly simultaneously as construction operations would permit in order to avoid exposure of the surfaces to low temperatures or to rapid fluctuations of temperature.

(4) Thickness of the Lifts and Time Interval between Successive Lifts. It is obvious that a thin lift of concrete, exposed on the top surface for a given period of time, will lose a greater percentage of the heat generated than will a thick lift exposed for the same period of time; so, if a fixed exposure period is established, temperature may be controlled by varying the thickness of the lifts. Similarly, for a fixed thickness of lifts, the temperature may be controlled by varying the exposure period. It has been found that when both the exposure period and the thickness are varied in such a way as to keep the average rate of construction constant (for example, at an average rate of one foot of depth per day) the ultimate maximum temperature rise of the concrete will not be greatly affected by the variations, although the thinner lifts show a slight advantage. However, under this condition of constant average rate, the temperature conditions during the very important early ages of the concrete are decidedly influenced by varying the lift thickness.

(5) Type of Forms and Time of Removal of the Forms. Although the control of temperature by varying the type and the time of removal of the forms has apparently not been used extensively in practice, recent studies indicate that this method may be an important one. It illustrates the importance of the control of temperature distribution as opposed to simple control of the maximum interior temperature. So far as thermal conductivity is concerned, 1½ inches of wood form may be equivalent to three feet of concrete. It is apparent that if the sharp break in the temperature gradient which occurs near the surface can be restricted to occur in the wood forms instead of in the concrete, a decided improvement may result. This might be accomplished in some cases by leaving the forms in place until the interior has cooled sufficiently to smooth out the break in the gradient. But if this procedure is not feasible, it may be advantageous to remove the forms as early as possible, say, at 24 hours after casting, so that the sudden temperature drop which occurs upon removal will take place when the high early plasticity of the concrete permits high strains without cracking. Also, in the case where forms must be removed early, this abrupt temperature drop at the surface might be avoided by employing a non-insulating form, such as one of sheet metal.

(6) Artificial Cooling. Cooling of the concrete by circulating cold water through embedded pipes represents one of the most important methods of improving temperature conditions. The method has the advantage that the cooling effect may be concentrated at locations where it is most needed, and may be turned on or off at will in order to maintain desired conditions. A cooling system having enough capacity to remove heat at the same rate at which it is generated in the concrete would solve nearly all the present temperature problems. Such a system would probably be too expensive to contemplate, but systems which approach this are a distinct possibility. Extensive systems, designed for the uniform cooling of entire massive dams, have been used very successfully; and more limited systems, intended only to improve conditions in certain selected parts of the structures, have recently been used with apparent success. The relationships between temperature and stress in concrete are not yet well enough understood to make possible the most efficient use of artificial cooling, but knowledge of this sort is being gained rapidly. Another function of cooling by embedded pipes is to accelerate the progress of cooling to the final stable temperatures, so that the contraction joints will attain their final openings, and may be sealed by injecting cement grout, within a relatively short time after completion of construction. A system installed for this primary purpose will also normally improve temperature stress conditions, especially if the circulation of the cooling water is started very soon after casting the concrete.

III. Temperature Measurements

Temperatures in the interior of concrete structures have been measured by mercury thermometers inserted into formed or drilled holes, and by thermocouples or resistance thermometers embedded in the concrete at the time of casting. Standard practice in this country has finally settled upon the copper resistance thermometer as the most satisfactory instrument. The copper wire coil is usually wound to a resistance of 46.40 ohms at 70 °F, giving a conversion factor of 0.10 ohm per degree, which is practically constant throughout the range of temperatures encountered in concrete structures. Instruments especially designed for embedment in concrete are now available. They show no significant change in calibration over a period of several years, and are sealed against the entrance of moisture under the continuous high pressures sometimes encountered in hydraulic structures. The resistance of the lead wires, which may be several hundred feet long, is eliminated from the resistance reading by using three-wire cables, so connected that the resistance of one pair of leads enters into each of two legs of the Wheatstone bridge. These cables are usually buried directly in the concrete, with no protective covering unless conduit is required for convenience in installation. It has been found that the better grades of commercial, rubber-covered, flexible cable show satisfactory performance over a period of several years when embedded in concrete.

The installations of thermometers are usually planned so that one or more typical sections of the structure will be covered quite thoroughly, thus providing a record covering several years of representative conditions of internal temperature. Additional instruments may then be installed for the investigation of particular problems, such as the measurement of the gradient in the vicinity of a water passage or other opening. In a large gravity dam, an adequate installation may require from one hundred to several hundred instruments, although significant results may frequently be obtained from much less extensive installations provided the instruments are properly placed for the investigation of selected problems.

IV. Temperature Computations

It should be apparent from the foregoing discussion that the methods and procedures customarily used in concrete construction work may be adapted to the exercise of some degree of control over temperatures without departing radically from ordinary practices. However, very little data are available to indicate the effect of the various procedures upon inherent stresses in actual structures, and until a considerable mass of such data becomes available it is essential that each new structure be considered as a new problem and be studied accordingly.

The first aspect of the problem should be a consideration of the stress-temperature relationships. A discussion of this aspect is not pertinent at this time; so it will be assumed that the designer knows the nature of the temperature distributions which he wishes to achieve, and the discussion will proceed to the methods which may be employed for comparing the temperature conditions which will result from various construction procedures.

The problem of the computation of concrete temperatures is a particularly satisfying one to the practical mathematician: first, because it is sufficiently involved to be intriguing; secondly, because the nature of the equations is such that cases of unlimited complexity may be built up from the simpler solutions; and thirdly, the complete development of the solution, the gradual elimination of transient terms, and the slow approach to the steady state may be followed in the mathematical procedure and may be accurately checked, step by step, by measurements in the interior of the structure. The problem consists of solving the differential equation of equilibrium in such a way that the boundary conditions are satisfied and the initial condition of temperature distribution is correctly represented. Solutions are now available which will handle a great variety of cases, but a large field still remains to be investigated.

Most present methods introduce two assumptions which are known to be inexact: (1) the thermal properties are constant throughout the range of temperatures encountered in a particular problem; (2) the surface temperature is the same as the ambient temperature. These assumptions are not required for solution of the problems, but are adopted because usually they do not introduce important errors, although the surface coefficient of heat transfer or the effect of solar radiation may be of considerable significance in some cases. In most cases, too, the direction of heat flow will be considered as linear. This involves the assumption that one of the surfaces is of infinite extent. Cases in which the intersection of two or more surfaces must be considered present no insurmountable mathematical difficulties, but computations involving distribution of temperature become very laborious.

The various methods of computing temperature distribution in the interior of a solid are based on the condition that at every point in the solid the curvature of the temperature gradient must be consistent with the time-rate of change of temperature; that is, in any element the difference in the rates of inflow and outflow of heat (together with the rate of heat generation, if any) must account for the rate of temperature change. This condition leads directly to the differential equation of thermal equilibrium as developed by Fourier. In its simplest form, representing the flow of heat in the x direction only of a rectangular coödinate system with no heat generation, the equation is:

$$\frac{\partial \theta}{\partial t} - h^2 \frac{\partial^2 \theta}{\partial x^2} = 0 \qquad (1)$$

where θ is the temperature and h^2 is the diffusivity. Solutions of this equation when applied to concrete structures represent the progress of cooling after heat generation has ceased, or they may represent the penetration of a change in surface temperature into the mass. These solutions assume particularly simple forms when the surface temperature is maintained constant, or when it may be represented by a sine curve. It is particularly important to note that the equation is linear, so that complex cases may often be treated by superposing the solutions derived for simple cases. The rigorous solution of Equation (1) with particular reference to concrete dams has been covered by Glover,[1] Vogt,[2] and others.

When heat generation within the mass is considered, the method of sources and sinks [3] may be applied to the solution of Equation (1). If a quantity of heat, Q, is liberated instantaneously at time $t = 0$ over each unit of area of the plane $x = x'$ of an infinite solid, the rest of the solid being at zero temperature, the temperature of the plane x at the time t is given by:

$$\frac{Q}{\sqrt{4\pi h^2 t}} e^{-\frac{(x-x')^2}{4h^2 t}} \qquad (2)$$

where the unit for Q is the quantity of heat required to raise the temperature of a unit volume by one degree. A continual supply of heat having the rate $d\phi(t')/dt'$

at time t' may be introduced by replacing Q by $d\phi(t')/dt'$, replacing t by $t-t'$, and integrating from $t'=0$ to $t'=t$.

The heat generation may then be spread over a finite depth by integrating again with respect to x', thus:

$$= \frac{1}{\sqrt{4\pi h^2}} \int_{x_1}^{x_2} \int_0^t \frac{d\phi(t')}{dt'} \frac{e^{-\frac{(x-x')^2}{4h^2(t-t')}}}{\sqrt{t-t'}} dt'dx' \tag{3}$$

Equation (3) applies to an infinite solid, but a boundary maintained at zero temperature may be introduced at a plane x_0 by assuming a reversal of conditions at this plane, so that the temperature at x_0 is maintained at zero degrees. Glover[4] has shown that the integration with respect to t' may be effected by a simple graphical method which has the added advantage that it does not require a mathematical expression for the rate of heat generation, $d\phi(t')/dt'$, but permits the direct use of the measured curve of adiabatic temperature rise.

By the use of Kelvin's solution, methods have been derived for handling a variety of complex conditions.[5] These particular solutions are restricted to cases in which only one boundary is involved, but they handle readily such cases as a succession of concrete lifts placed on a rock foundation and exposed to varying air temperatures.

For cases in which it is desirable to express the heat generation curve by an equation, the following expression has been used:

$$Q_t = Q(1 - e^{-rt}) \tag{4}$$

where Q is the total amount of available heat and r is an experimental constant. The equation expresses the condition that the rate of heat liberation is at all times proportional to the amount of available heat remaining. If a single term of this type does not correctly represent the heat generation curve, two or more such terms may be used, in accord with the linear nature of the equation of equilibrium.

When rigorous solutions are required for a body of finite dimensions, Fourier's method may be applied. If the rate of heat generation is included in the equilibrium conditions, Equation (1) becomes:

$$\frac{\partial\theta}{\partial t} = h^2 \frac{\partial^2\theta}{\partial x^2} + \frac{1}{c}\frac{dQ_t}{dt} \tag{5}$$

where Q_t/c is the adiabatic temperature rise of the concrete. The curve of temperature distribution at any time may be expressed as a series of sine and cosine terms, each multiplied by a coefficient which is a function of the time; and Q_t may be expressed in terms of Equation (4). By differentiating and substituting in (5), a series is obtained containing coefficients which may be evaluated by the usual methods for Fourier's series. For the case of a slab of infinite thickness and width but of finite length, initially at a temperature of 0° and exposed at the ends to a constant temperature of 0°, the temperature equation is:

$$= \frac{4rQ}{\pi c} \sum_{1,3,5\,\cdots} \frac{e^{-rt} - e^{-n^2h^2t}}{n^3h^2 - nr} \tag{6}$$

where the unit of length has been chosen for convenience so that the length of the slab is equal to π. A conversion to any other length, l, involves only multiplication of all linear dimensions in the equation by π/l. If the heat were generated instantaneously, r would become infinite and the quantity Q/c would represent a uniform initial temperature θ_0; Equation (6) then reduces to the well known form for simple cooling without heat generation:

$$\theta = \frac{4\theta_0}{\pi} \sum_{1,3,5\,---}^{n=\infty} \frac{e^{-n^2h^2t}}{n} \sin nx \tag{7}$$

Many fundamental cases can be solved by the use of Equations (6) and (7). The series converge rapidly for large values of h^2t, but converge rather slowly when h^2t is small, which makes the computation very laborious for determining conditions shortly after casting.

A very satisfactory and simple method applicable to almost any condition of one-dimensional flow and to simple cases of two-dimensional flow has been developed by Carlson.[6] Essentially the method consists of solving the differential Equation (5) when expressed in terms of finite increments, so that during successive time intervals the temperature change in each element of length is consistent with the temperature gradients at the boundaries of the element. The computation proceeds step by step by means of a tabular arrangement, so that the temperature in each element is determined at the end of each interval of time. The complications introduced by such factors as variation in ambient temperature, differences in thermal properties of adjoining materials, and so forth, are readily handled.

The ingenious step-by-step method developed by E. Schmidt[7] may readily be extended to cover the case of internal heat generation. In the case of simple cooling, with one-dimensional heat flow, the rate of temperature change of any interior element depends only on its own temperature and on that of the two adjoining elements. Thus, the change in temperature distribution during a sufficiently small interval of time may be determined approximately by considering successive groups of three elements, each group being independent of the others. If the nature of the curve of temperature distribution is such that derivatives of fourth and higher order are not significant, a very simple relationship may be established within each group; for if the time and space intervals are so chosen that the relationship $\Delta t = \overline{\Delta x}^2/2h^2$ is satisfied, and if θ_p, θ_q, θ_r are the temperatures of three successive points at the beginning of a time interval, at the end of the interval

$$\theta_q + \Delta\theta_q = \tfrac{1}{2}(\theta_p + \theta_r) \tag{8}$$

The computation procedure consists merely of writing out the initial temperature distribution and averaging alternate terms. If heat is being generated, the amount generated during each interval, expressed as degrees of adiabatic temperature rise, may be added after averaging. Although the diffusivity of concrete varies considerably, 1.0 square foot per day is a fair average, and this gives intervals of one foot and one-half day as convenient values which satisfy the necessary relationship for Schmidt's method.

The equations for the cooling of hollow cylinders are of considerable importance, for in cases where the temperature is controlled by circulating cold water through pipes embedded in the concrete, the pipes are usually so spaced that each one may be considered as lying along the axis of a hexagonal prism. No significant errors are introduced if the prism is then considered as a cylinder of the same cross-

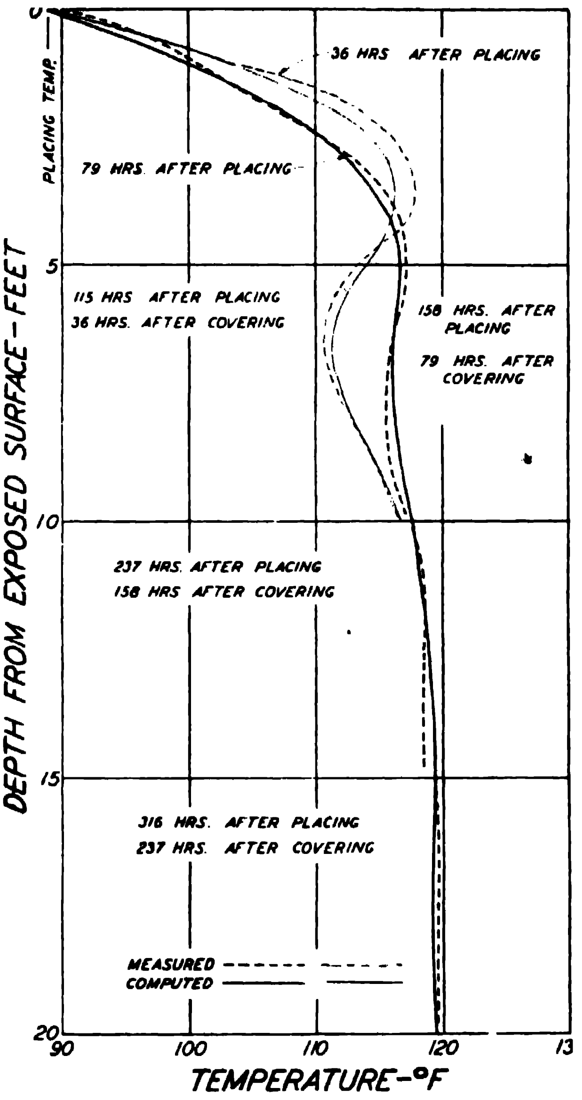


FIG. 2.

sectional area. The equation of thermal equilibrium in cylindrical coördinates, without heat generation, reduces to:

$$\frac{\partial\theta}{\partial t} = h^2\left(\frac{\partial^2\theta}{\partial r^2} + \frac{1}{r}\frac{\partial\theta}{\partial r}\right) \tag{9}$$

when the initial and boundary conditions are functions of r and t only. Solutions may be reached by setting:

$$\theta = e^{-h^2\alpha^2 t}u$$

where u is a function of r. By forming the required derivatives, it is found that:

$$\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} + \alpha^2 u \quad 0$$

which is Bessel's Equation of zero order. Solutions which satisfy the initial and boundary conditions may be built up in a manner similar to that employed in the determination of Fourier's series. Such solutions represent the condition of cooling from a given initial temperature distribution, and in such form they have been valuable in estimating the effectiveness of cooling systems, the proper spacing and diameter of pipes, and so forth. In cases where the factor of heat generation must be taken into account, approximate solutions may be built up by assuming that certain increments of heat are liberated instantaneously at successive times, thus setting up a succession of "initial" conditions. The results of the sequence of computations may then be added together to give the final results.

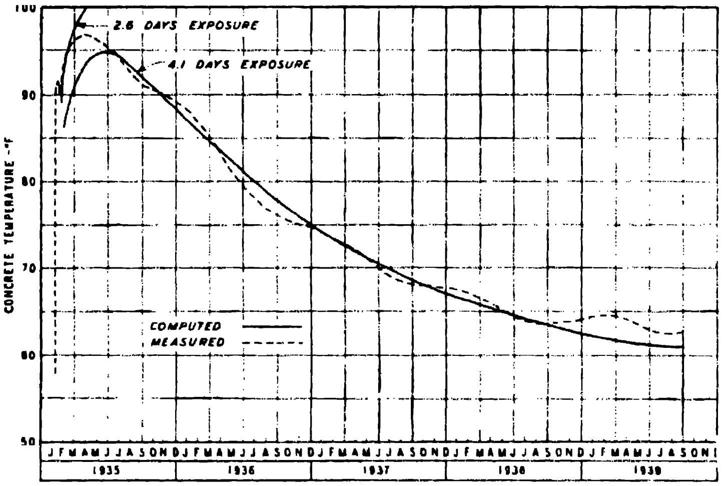


Fig. 3.

V. Comparison of Measured and Computed Temperatures

In general, precise agreement is not to be expected between measured and computed temperatures; but comparisons of the two have indicated that for many cases a degree of accuracy in the computations may readily be attained which will amply satisfy the majority of engineering requirements. The curves of Fig. 2 give a typical comparison. They represent the measurement and computation of the vertical distribution of temperature through four 5-foot lifts of concrete in Norris Dam at a considerable distance from the foundation and the exposed faces. The maximum discrepancy is about 2°. Actually, the measurements were made in only one lift, but since the exposure periods of the lifts were reasonably uniform, the diagrams, when placed one below another, may be considered as representing conditions in a succession of lifts. The discontinuities in the curves of measured temperature are due to variations in the exposure periods. This computation was made by Schmidt's method, using time intervals of two hours for the first 18 hours after casting each lift, and of nine hours thereafter.

Fig. 3 shows the temperature history during a period of four and one-half years of a point in the interior of Norris Dam, located 46 feet from the nearest exposed face. The lift containing the thermometer was exposed 2.6 days, and the average exposure of several lifts above and below was 4.1 days, so the computation was made for the two cases in the expectation that the first curve would prevail for the earlier ages and the second curve for the later ages. The computations were by Fourier's series, using a constant surface temperature equal to the mean annual air temperature. The effect of the variable surface temperature might, of course, be readily superposed if required. The discrepancies between the measurements and the computations may be accounted for principally by the numerical data introduced into the equations. It appears from the curves that the value used for the diffusivity was slightly low, and that the mean surface temperature was actually somewhat higher than the mean ambient temperature.

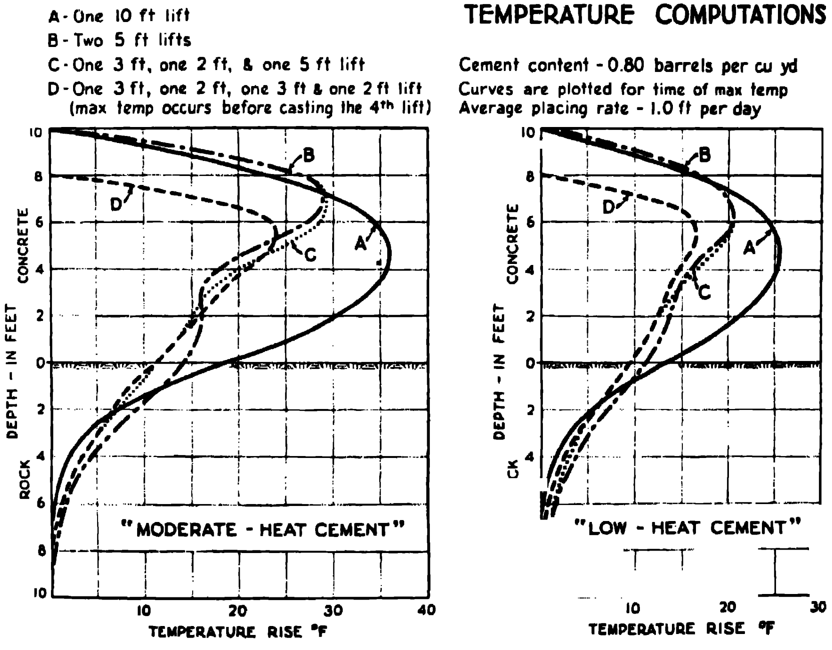


FIG. 4.

Additional data from the Norris Dam measurements have been published elsewhere.[8] Comparisons in which the effect of heat generation have been included have also been published by the United States Bureau of Reclamation[9] and by Nielaender.[10] The general conclusion drawn from these comparisons is that the mathematics of the temperature computations is unquestionably sound. Errors are introduced when the actual physical conditions do not represent those assumed in the derivation of the equations, but these errors may be reduced to negligible amounts by the exercise of reasonable discretion in choosing the computation methods. Errors of greater significance may result from the empirical data which are substituted in the equations. It is particularly important to know accurately the diffusivity of the concrete and the rate of heat generation of the cement.

VI. Typical Application of Temperature Studies

A typical result of the computation of temperature distribution is shown in Fig. 4. The problem in this case was that concrete was to be placed at an average predetermined rate of one foot of depth per day, but some choice was offered in thickness of lifts and time of exposure of the lifts. If 10-foot lifts were used, they would be exposed for ten days before covering; if 5-foot lifts were adopted, the exposure period would be five days; and so forth. Also, the cement might be either a moderate-heat or a low-heat type. The computation was made by Carlson's method for the first 10 feet of concrete above the foundation as cast in 1, 2, 3, or 4 lifts, and the curves were plotted for the particular time at which each of the four casting methods showed its maximum temperature. The figure indicates that by the use of these two controls—type of cement and thickness of lifts—the maximum temperature rise near the foundation may be varied between the limits of 16 and 36 °F, even though no change was made in the rate of construction.

Carlson[11] has published rather extensive temperature computations, together with suggestions for the application of the data.

As mentioned previously, the ultimate problem involves the control of thermal stress, and in this respect the evaluation of the curves of temperature distribution requires considerations which fall outside the scope of the present discussion.

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Thermometers for Aircraft

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Thermometers are used on airplanes to measure the cylinder-head temperatures of air-cooled engines, the temperature of the lubricating oil of air-cooled engines, or of the coolant of liquid-cooled engines, the temperature of the carburetor air, and the free-air temperature. On airships the difference between the temperature of the lifting gas and of the free air, known as the superheat, is measured. The free-air temperature above the surface of the earth is now measured daily at many meteorological stations by means of a temperature element forming part of a radiosonde.

Three types of distant indicating instruments have been or are being used to measure the temperature, usually in the range −10 to +120 °C, of the lubricating oil or coolant of aircraft engines: the liquid-filled thermometer, the vapor-pressure thermometer, and the electrical resistance thermometer. The liquid-filled type is now but little used; descriptions and performance data are given by E. F. Mueller and R. M. Wilhelm,[1] and briefly by Harcourt, Sontag and W. G. Brombacher.[2] The vapor pressure type is now most commonly used with various lengths of capillary tubing up to 40 feet. Sontag and Brombacher [2] have described the instrument and have extensively discussed its performance from the aeronautic point of view.

The vapor-pressure thermometer is now being displaced for this use by the resistance thermometer, because the latter can be more quickly installed and removed during overhauling operations, and also because the length of the electrical leads is not as limited. The design of the resistance thermometer is to be such that it can also be used for measuring carburetor air and free-air temperature. At present the resistance bulbs are sealed in metal or glass with the maximum dimensions standardized. The heat capacity of the bulb is made small in order to minimize the lag. The bulb resistance is 100 ohms at 0 °C. The Wheatstone bridge and the electrical indicator are housed in the same case. The supply voltage is either 14 or 28 volts, the latter now preferred, maintained at the selected value by means external to the instrument. Present specifications of the Bureau of Aeronautics, Navy Department, specify the accuracy at indicator temperatures between −35 and +45 °C, the current consumption of the instrument, the permissible effects of vibration and the time lag constant of the bulb. Tests for ruggedness and leak-tightness under service conditions of use and misuse are also required. The time lag and its variation with air density (altitude) and circulation of the medium in which the bulb is immersed, and the temperature rise as a function of the energy input into the bulb have been discussed by John B. Peterson and S. H. J. Womack.[3] The data given are of particular value when the instrument is used to measure air or other gas temperatures.

For measuring engine cylinder-head temperatures the combination of a thermocouple and millivoltmeter is being used. The indicators have a range from 0 to 350 °C. In a few large airplanes a potentiometer developed for the purpose is used instead of the millivoltmeter. The greater weight of the potentiometer is more than compensated by the saving in weight of the leads thus made possible. Descriptions and performance data are given by Peterson and Womack.[3]

Routine measurements of free-air temperatures are made in airplanes for the purpose of determining the probability of icing, for correcting altimeter readings for the effect of air temperature, and reducing indicated air speed to true air speed. Vapor-pressure or bimetal thermometers are much more commonly used than the liquid-filled distant-indicating and liquid-in-glass types. The use of electrical resistance thermometers, as discussed above, promises to be more general in the near future. The vapor-pressure instrument commonly has a range from −40 to +50 °C, has a comparatively long bulb, and has an indicator installed in either the standard 1⅞- or 2¾-inch dial size case. The filling liquid is commonly dichlorodifluoromethane (Freon). In laboratory tests under expected conditions of use the errors are ordinarily less than 2 °C, and less than 1 °C at temperatures near 0 °C where the highest accuracy is specified.

The bimetal thermometer is designed to be fastened to the airplane structure at a location where it is exposed to the free air. It is graduated in the range −40 to +40 °C on a 2¾-inch dial in order to facilitate reading it from the cockpit of the airplane. The bimetal operates the pointer without intermediate gearing or levers. For quick response to temperature changes, experimental instruments have been made with screened openings in the case to permit ventilation of the bimetal coil. The specifications required an accuracy of 1 °C in the range −25 to +30 °C, and 2 °C at other readings.

In the flight testing of aircraft the free-air temperature is measured with resistance thermometers, which differ from the instrument described above in that provision is made for adjusting the supply voltage and that an indicator with a greater openness of scale is used. The instruments used by the Bureau of Aeronautics, Navy Department, are discussed fully by Peterson and Womack.[3] The Army Air Corps uses a similar instrument with some modifications. The range now standard for the Bureau of Aeronautics is −75 to +45 °C. The overall accuracy is at least ±1 °C.

In airship operation superheatmeters are essential. There are two types, one in which thermocouples are used, and the other in which electrical resistance elements are employed. The latter type is the more satisfactory in view of the difficulty of obtaining a satisfactory indicating instrument for the thermocouple superheatmeter owing to the long lines required. These instruments are also discussed by Peterson and Womack.[3]

The electrolytic thermometer forming part of radiosondes used by the Weather Bureau and U. S. Navy in making upper air soundings are discussed by Christos Harmantas in this Symposium. Alternative methods of recording temperature which are still used to some extent are the Jaumotte meteorograph and the common type of meteorograph. The Jaumotte instrument[4] consists of a pressure element and a bimetal temperature element so arranged that a stylus records on a smoked plate the temperature against the pressure. In the common type of meteorograph, made by Julien P. Friez and Sons in this country, the deflections of a bimetal element are recorded by a stylus or pen on a clock-driven drum, together with the air pressure and relative humidity.

Finally, attempts to establish international altitude records are made under regulations issued by the Fédération Aéronautique Internationale (F. A. I.). The free-air temperature must be recorded in these flights since it enters into the computation of the altitude. Methods of recording the free-air temperature under these regulations have been discussed by W. G. Brombacher.[5]

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Standardization of Thermometric Methods in Great Britain

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Since the end of the nineteenth century, boiler, furnace and engine tests in Great Britain have usually been based upon the reports of the Heat Engine Trials Committees[1] of the Institution of Civil Engineers. In 1935, it was agreed between the Institution and the British Standards Institution that the latter body should underake the codification of test schedules. A series of Committees was established to draw up schedules of test for steam boilers, ferrous and non-ferrous furnaces and various types of ovens, kilns and dryers, carbonization retorts and other heat-using plants. In the course of their work, these Committees found it necessary to lay down methods of determining the basic physical magnitudes, particularly gas flow and temperature data. It was recognized that it would be difficult for a number of specialized committees working separately to adopt uniform procedure for these measurements; and a select committee of the B. S. I. on which the National Physical Laboratory and other branches of the Department of Scientific and Industrial Research were represented, recommended that a representative Technical Committee should be set up by the British Standards Institution to draw up codes for gas flow and temperature measurements. Mr. J. G. Bennett was appointed Chairman of this Committee, which in turn set up two sub-committees to deal respectively with temperature and flow data. Mr. Bennett undertook the chairmanship of the first, and Mr. Reber, of the Woodall-Duckham Companies, that of the second.

The Technical Subcommittee, described as British Standards Institution Subcommittee SF/9/1, Temperature Measurement, with a membership of thirty-three engineers and scientists, is fully representative of the makers and users of thermometric instruments and of the scientific workers who have carried out research in this field. It was hoped that earlier reports on temperature measurement might be adopted as the basis of the Committee's work, but a careful review of the literature made it clear that no document existed dealing with the particular problem with which the Committee was faced. Authoritative recommendations for the determination of the fixed points of the International Temperature Scale were available in the reports of the International Committee of Weights and Measures, and in the publications of the National Physical Laboratory.[2] The problem, however, was to relate the temperatures as determined in the laboratory on the International Temperature Scale with the conditions of industrial practice, for it must be remembered that the aim of the Committee's work was to provide engineers engaged in testing heat-using equipment with reliable methods of temperature determination.

There is a fundamental difference between the conditions under which the fixed points of the International Temperature Scale are determined in the laboratory and those of temperature measurement in industry. In the former case, the most careful precautions are taken to insure thermal equilibrium between the test bodies under comparison, since temperature as defined on the thermodynamic scale has an unambiguous meaning only for a system in thermal equilibrium. On the other hand, the essential purpose of an industrial furnace is to evolve heat and transfer it to some medium or product as completely, and usually as rapidly, as possible.

It follows that nothing approaching thermal equilibrium is present in any part of an industrial heat-using system, and the methods of measuring temperature must take this basic fact into account.

Discussions which took place in 1937 among technical representatives of the British coal and steel industries, who were seriously disturbed by the difficulties of securing reliable gas-temperature measurements, led to the suggestion that the Institute of Fuel should be invited to organize a symposium to discuss the particular problem of gas-temperature measurement under industrial conditions. This Symposium, which was held on December 2, 1938,[3] is viewed in a separate communication to the present meeting. It may be said that the most striking feature of the Symposium was the emphasis laid, in almost every page, on the difficulties of measuring temperature under conditions of thermal flux.

B. S. I. Subcommittee SF/9/1 agreed, therefore, to build up its Temperature Measurement Code around the problem of temperature determination in the presence of a flux of heat. The British Coal Utilization Research Association, which had been making a special study of this problem in connection with boiler furnaces, pulverized-fuel firing, and large-scale producer gas transmission, undertook to prepare a draft which was submitted to the Committee by Mr. J. G. Bennett and Mr. M. W. Thring on January 25, 1938.[4] The chapter headings of the draft specification indicate the general scheme:

Section 1. General
  Sub-Section A. Introduction.
  Sub-Section B. Classification of Thermometric Methods.
  Sub-Section C. General Principles of Temperature Measurement.
  Sub-Section D. Sources of Error and Precautions to be Taken.
  Sub-Section E. Summary of Characteristics of Thermometric Methods.

Section 2. Expansion Thermometers.
Section 3. Electrical Resistance Thermometers.
Section 4. Thermocouples.
Section 5. Radiation Pyrometers.
Section 6. Change of State of Test Body.
Section 7. Electrical and Other Auxiliary Instruments.
Section 8. Temperature in Interior of Solids.
Section 9. Temperature at the Surface of Solids.
Section 10. Temperature of Liquids.
Section 11. Temperature of Gases.
Section 12. Calibration and Testing.

It may be of interest to give further details of Section 1B, dealing with the classification of temperature measuring instruments.

Group I. Contact Methods

This includes the whole group of contact thermometers, the operation of which depends on the fact that the thermal transfer between the hot body and the testing body continues until such time as the mean kinetic energies of the ultimate particles of each are equal. The testing body is placed in contact with the hot body.

Class A. Thermal Expansion of Test Bodies

This class includes all thermometers in which thermal expansion of a solid, liquid or gas is directly measured.

Type (i). Expansion of Solids
  Sub-type (a). Solid rod thermometers.
  Sub-type (b). Metal coil thermometers.
  Sub-type (c). Bimetallic strip thermometers.

Type (ii). Liquid Expansion Thermometers
  Sub-type (a). Mercury, alcohol, etc., in glass thermometers.
  Sub-type (b). Mercury, alcohol, etc., in metal thermometers.

Type (iii). Gas Expansion Thermometers
  Sub-type (a). Constant pressure thermometers.
  Sub-type (b). Constant volume thermometers.

Class B. Thermoelectric Junctions

Type (i). Base-metal thermocouples
Type (ii). Precious-metal thermocouples

Class C. Electrical Resistance Thermometers

Class D. Radiation from Test Body Placed in the Gas*

Class E. Change of State of a Test Body

Type (i). Melting Point Methods
  Sub-type (a). Substances of fixed melting point.
  Sub-type (b). Seger or Orton cones.
Type (ii). Boiling-point Methods
Type (iii). Vapor-pressure Methods

Class F. Calorimeter Pyrometers

Class G. Special Methods Designed to Obtain Temperature Equilibrium between Test Body and Hot Body

Type (i). Suction Pyrometers
Type (ii). Methods in which additional heat is supplied

Group II. Non-contact Methods

In this group, the testing body is generally placed at a distance from the hot body and constitutes some form of radiometer. The method is generally applied to measurement of surface temperatures of solids and fluids. It is also used indirectly for the measurement of gas temperatures when a solid testing body is placed in the gas.

Class A. Black Body Radiation Measurement

Radiation may be made effectively black body by the use of hollow emitters; or, in certain cases, the existing surface is a reasonably good approximation.

Type (i). Total Intensity Radiometers
  Sub-type (a). Thermojunction heating elements.
  Sub-type (b). Bimetallic strip heating elements.
  Sub-type (c). Resistance wire heating elements.

*The temperature of the body is measured by means given in Group II, but it is given here as thermal equilibrium is reached by the transfer of molecular energy.

Type (ii). **Optical Pyrometers**

Sub-type (a). Pyrometers in which a match is made by varying the intensity of the local source. Filament pyrometers.

Sub-type (b). Pyrometers in which the relative amounts of light coming from fixed sources are adjusted. Polarizing pyrometers. Wedge pyrometers.

Type (iii). Photoelectric Tube Pyrometers

Class B. Instruments Designed To Give Correctly the Temperature of a Grey Body*

Type (i). Color pyrometers or pyrometers which depend upon the comparison of the intensities at two wave-lengths.

Type (ii). Comparison of black body and color temperatures

Class C. Electron Excitation Radiations from Solids and Gases

Temperature measurements depending on the observation of spectral lines, *e.g.*, the sodium line reversal method.

Dr. Margaret Fishenden and Dr. O. Saunders undertook to elaborate Sub-Section I D, dealing with sources of error,[5] and a sub-committee under Mr. A. J. Philpot, Director of the British Scientific Instrument Makers Research Association, drafted Section 7 relating to electrical instruments. Mr. Blackie of the Fuel Research Station drafted Section I C dealing with general principles.

The following panels dealt with Sections 2-6:

Section 2: Expansion Thermometers: Mr. R. Harrison of Negretti & Zambra Ltd.

Section 3: Electrical Resistance Thermometers: Mr. S. Wakeham, Cambridge Instrument Company.

Section 4: Thermocouples: Mr. C. E. Foster, Foster Instrument Company

Section 5: Radiation Pyrometers: Mr. R. W. Griffin, Elliott Brothers Ltd.

Section 6: Change of State of Test Bodies: Mr. E. Rowden, British Refractories Research Association.

A second draft embodying the results of the work of the various subcommittees and panels was completed early in 1939 and was circulated for comment to a small number of selected workers in Great Britain. A large number of valuable suggestions and comments were received and the Committee considered these during the spring and summer of 1939. At the present time, a third draft has been completed, which, after revision by the Main Committee, will be circulated for comment to interested workers at home and abroad. Mr. Bennett, as Chairman of the Committee, will be glad to receive through the American Institute of Physics the names of any American workers or organizations who may desire to receive the revised draft code, which, it is hoped, will be completed early in 1940.

*A grey body is defined as a source of radiation whose emissivity differs from unity, but whose radiation intensity distribution with respect to wave-length is the same as that of a black body.

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Chapter 10

Metals and Ceramic Industries

The Measurement of Open-hearth Bath Temperature

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Need of a Method for Routine Use

For many years the steel industry has felt the need for an accurate method of measuring the temperature of liquid steel in the open-hearth furnace.

At first glance it might appear that the temperature of the liquid bath is of little importance, so long as it is high enough to permit the metal to be tapped out of the furnace and subsequently poured into molds. Both experience and theory, however, show that the temperature is a vital variable. Oxygen is an influential constituent of steel, and the solubility of oxygen in the liquid rises very rapidly with temperature. The chemical reactions between metal and slag, and also among the constituents within the metal bath itself, never entirely cease, and their rate can be doubled by a small rise in temperature. The crystalline structure of the solid metal, the perfection of surface on the ingot, and the amount of segregation of minor constituents during freezing, all are influenced by the temperature of the liquid when it is poured into the mold. Finally, evidence is accumulating to the effect that the temperature to which a liquid metal has been heated affects the character of its crystallization when it is again cooled to the freezing point. For these and other reasons it is desirable to know the temperature of the open-hearth bath within a few degrees.

The specifications for this temperature measurement are severe. The instrument must be portable enough to be moved quickly out of the way to clear the floor for charging and similar work. It must be rugged enough to stand steel-mill conditions, in which dust and vibration are the principal risks. It must make an automatic record, independent of any personal equation. Preferably, it should not require highly experienced personnel to operate successfully. Finally, it must do a better job than is now being done by the melter's trained eye.

The last sounds easy until it is tried. An experienced open-hearth melter is able to make a fairly good estimate of the temperature of his metal without the aid of any pyrometer. He does it by observing the activity of the reaction between slag and metal, the brightness of the slag surface, the effect of the metal on an inserted steel rod, the brightness of the liquid metal when poured from a sampling spoon. He is helped by his blue glasses, which are not merely protective but act as a color pyrometer. Although these methods are all subjective, yielding no record in figures, there is no use in trying to replace them with an instrumental record that is good only to ±25 or 50 °F. We need to set our ambition on temperatures that are at least reproducible to ±10 °F (6 °C) and if possible accurately measured within that range of tolerance. Furthermore, the pyrometer must be one that can be used without interfering too much with the melter's regular work, or consuming too much of his time. We shall then have something really usable in controlling the furnace and the quality of the steel.

The liquid metal is inaccessible to direct observation in the furnace because of its covering of liquid slag. It is true that its temperature can be read with an optical pyrometer while the metal is being tapped into the ladle and again while it is being poured from the ladle into the ingot molds. These readings are in themselves quite precise, especially the readings of pouring temperature, but they are subject to a large correction for the emissivity of the metallic surface; at an apparent temperature of 2700 °F this correction amounts to +250 °F, using the generally accepted emissivity of 0.4, yielding a true temperature of 2950 °F. There is no objection to adding a large correction provided we are sure of it, but it is unlikely that emissivity is independent of composition, even though pure iron and iron containing several per cent carbon appear to have the same emissivity. We know already that the emissivity is measurably increased by certain alloying elements such as manganese and chromium and it may, for all we know, be affected by the gases escaping from a flowing stream. Furthermore, the readings are obtained when the metal is already out of the furnace or the ladle, when little can be done to change or control the temperature.

Comparison of Methods

In view of the importance of this subject to the open-hearth process, one of the authors (Sosman), with the aid of pyrometrists from several steel plants, conducted a ten-day comparison of methods for open-hearth bath temperature at the Pencoyd Works of the American Bridge Company in 1936. The methods compared were:

(1) Dissolving-tube method, using a platinum thermocouple encased in porcelain and graphite.
(2) Test-spoon method.
(3) Bath-equalization method of Larsen and Shenk.
(4) Rod-boil method.
(5) Slag-bubble method.
(6) Slag-surface method.
(7) Collins-Oseland tube method.

Our conclusion from this series of comparisons was that the Collins-Oseland tube held the most promise of becoming a practical and dependable method for routine use, although quite reliable readings were also obtained with the test-spoon when the procedure was carefully standardized.

Description of Methods

1. Dissolving-tube Method. A platinrhodium-platinum thermocouple is inclosed in a small porcelain tube of $\frac{3}{16}$-inch (5-mm) bore and $\frac{1}{16}$-inch (1.5-mm) wall. This is about as small and thin a tube as can be handled, and its use in the steel bath is rendered possible only by encasing it (loosely) in a graphite tube (Acheson artificial electrode graphite) $1\frac{3}{4}$-inches O. D. and 14 inches long, tapered for 4 inches at the closed end down to a diameter of $\frac{1}{2}$ inch. The graphite tube with its inclosed porcelain tube and thermocouple is set in a water-cooled head, and the thermocouple wires are led out through a pipe inside one of the two water pipes. An essential detail is a packing of asbestos cord around the porcelain in the opening of the graphite sheath to prevent the rise of gases which would carry spurts of steel up into the water-cooled head after the graphite has begun to dissolve away. (See Fig. 1.)

The combination is inserted through a door of the furnace, with a sheet-metal shield protecting the operators. When immersed in the steel bath, the graphite quickly dissolves away below the slag level, leaving the porcelain in direct contact with the liquid metal and immersed therein to a depth of 6 to 8 inches. Within the slag layer the graphite remains to protect the porcelain. Readings of the emf of the couple are made with a semi-precision, portable potentiometer, and can be continued for several minutes before the porcelain begins to be attacked by dissolved FeO or to bend under the lifting force of the liquid. If withdrawn in time, the couple can be used repeatedly, but there is evidence that either carbon monoxide or iron vapor penetrates the porcelain and gradually contaminates the couple. To secure an accuracy of 5 °F in the temperature of the metal at the point of immersion, the couple should be used only once or twice. We found that inequalities in the metal bath itself far exceeded the range of accuracy of the thermocouple reading.

Since these experiments were made, the British Iron and Steel Institute's Subcommittee on Liquid Steel Temperature[1] has used a similar thermocouple method, but with a vitreous silica protection tube and no graphite covering. Their supporting tube was not water-cooled, but was protected by a porous insulating refractory. The pyrometer was used principally in the acid open-hearth, in which the slag is highly siliceous and therefore not so corrosive to silica as the basic open-hearth slag is.

Our method with the thermocouple and water-cooled head gives dependable results, at least in a killed steel bath, and will be used again as a basis for further standardization of the tube method which is now in practical use, and which is to be described later.

In an active bath or in a ladle of rimming steel, in which there is always a vigorous evolution of gas around any inserted colder object, it is doubtful whether a true temperature can be obtained with an immersed tube. Heat is being absorbed or released at the point of measurement, and therefore the couple temperature cannot exactly equal that of the mass of metal. This point was brought out in a recent discussion of bath pyrometry[2] and should receive further experimental study.

The thermocouple or dissolving-tube method as used at Pencoyd is too awkward and expensive for plant routine control, and is, furthermore, dangerous because of the presence of inclosed water near liquid steel.

2. **Test-spoon Method.** Metal is held in or poured from a slag-coated test spoon, and the temperature of the dark liquid in the spoon is read with an optical pyrometer. A correction for an emissivity of 0.4 must be added to obtain true temperature.

Not all test-spoon readings are satisfactory. Only when the slag is thin enough to permit the dipping of a clean sample in a properly slagged spoon can the reading be taken. If the slag is lumpy or viscous the readings are unreliable. To obtain satisfactory readings, a routine of slagging, dipping, removing from furnace, and reading, must be adhered to with rhythmic precision, for the metal cools so rapidly that even half a second's departure is significant. With an experienced reader, however, it was surprising to see how consistent the results can be.

Satisfactory readings by this method could not be obtained with a disappearing-filament optical pyrometer. Only the type in which the brightness of the object is varied to match a small spot of constant brightness could be successfully used, because of the necessity of finding the target quickly and matching it almost immediately. Our readings by this method, though self-consistent, proved, when corrected for an emissivity of 0.4, to be 20 to 30 °F higher than the probable true temperature.

3. **Bath-equalization Method.** In the course of their development work on the photoelectric roof pyrometer, Larsen and Shenk tested the principle of letting the open-hearth furnace come to radiative equilibrium and then measuring its temperature automatically.

A photoelectric roof pyrometer was sighted on the inner surface of the roof through an opening in the back wall. Another pyrometer of the same type was sighted downward through a water-cooled opening in the roof upon the slag surface. The two pyrometer circuits were connected in opposition, with a relay also in the circuit which would turn on the fuel as soon as the difference between the two pyrometers fell below a certain set maximum of 10 or 20 °F.

The procedure in taking a bath temperature was to shut off the fuel and air supply, throw in the relay circuit, and wait. Within a period of 15 to 50 seconds the slag, if not too viscous, would presumably have attained the temperature of the large mass of metal beneath it, in which most of the heat in the furnace is stored; at the same time the roof and slag would be equalizing in temperature by radiation, a process which is very rapid at this high temperature. When metal, slag, and roof become equal in temperature within the prescribed tolerance, the fuel and air are automatically turned on. Meanwhile, the recorder of the roof pyrometer has been registering the roof temperature, and its minimum, shown on the record when the returning flame causes a sudden rise, is the equalized bath temperature.

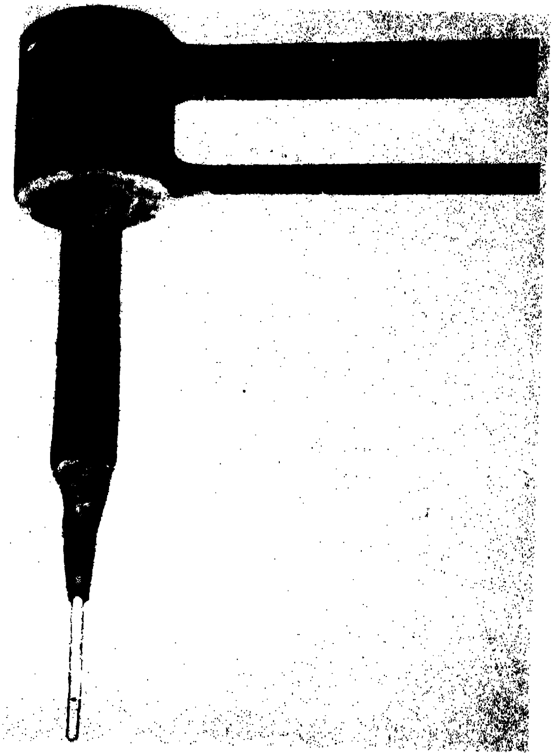

FIG. 1. Dissolving-tube pyrometer after a reading in an open-hearth bath, showing thin porcelain protection tube exposed by dissolution of the graphite in the steel, while protected by the graphite within the slag layer.

The bath temperature obtained in this way is in the nature of an average surface temperature, and if the bath is not homogeneous, readings at individual points, such as are obtained with thermocouple or spoon, will differ from it. This is probably the reason why we found that the equalization method gave a terminal temperature (just before tapping) that appeared more nearly correct than any other method, yet was more erratic than the results by the tube method which has the effect of stirring the bath vertically within a restricted area.

During the heats, the equalization temperature was 20 to 30 °F above the probable true temperature. Its precision is high, about ±5 °F. When more than one equalization temperature was taken during the tapping period, the furnace temperature was found to be diminishing at such a rate that it lost 5 to 10° during the four- to six-minute tapping period.

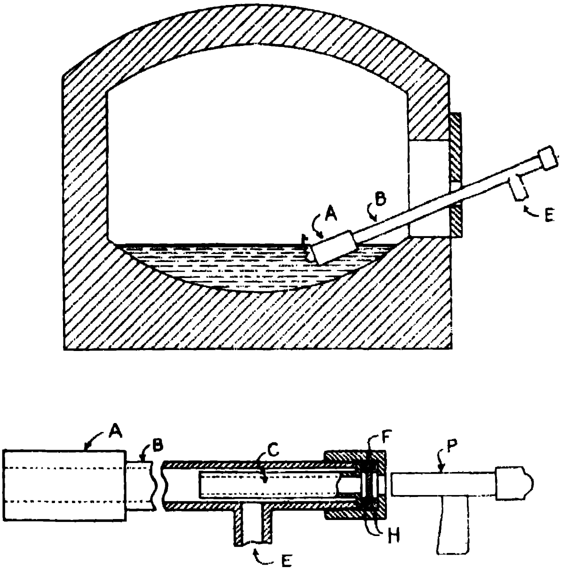

FIG. 2. Collins-Oseland tube as used at Pencoyd (drawings adapted from U. S. Patent 2,030,019).

A. Welded steel tip.
B. Pipe.
C. Inner pipe to protect window against moisture and dirt.
E. Connection for introduction of air.
F. Glass window.
G. Air-tight cap, carrying window.
H. Asbestos gaskets.
P. Optical pyrometer.

4. **Rod-boil Method.** A cold steel rod is inserted through the wicket into the bath while it is still active, and an optical pyrometer is sighted on the surface of the metal as it boils up through the slag. (The boiling is caused by the escape of carbon monoxide from solution as a result of the local chilling.) Readings are made during reversal of the furnace, when the flame is off. There is no correction for emissivity. The few readings which it was possible to secure by this method were consistent with the equalization and the test-spoon methods.

5. **Slag-bubble Method.** An optical pyrometer reading is made, during reversal, on the interior of a gas bubble just as it bursts. The slag surrounding the bubble has just risen from the surface of the metal, presumably carrying the metal temperature with it, and in fact the bubbles can often be observed to be

appreciably darker than the main body of slag. This indicator of metal temperature was suggested by Mr. Larsen.

The relatively small number of readings that we made by this method were, like the rod-boil temperature, consistent with the equalization and the spoon methods.

6. **Slag-surface Method.** The temperature of the bath is inferred from a series of optical pyrometer readings during reversal, on the brighter areas of the slag as the bath is heated up toward the end of a heat. There is no emissivity correction. The results by this method, as might be expected, could not be used as a basis for estimating the true temperature of the bath, even though they were useful in showing the general course of temperature increase as influenced by fuel input and other factors.

7. **Collins-Oseland Tube Method.** The liquid steel is observed with an optical pyrometer through an open tube which is inserted into the liquid and is kept clear by a current of air. The method was developed by Carl Oseland and F. L. Collins in 1936 at the Gary Steel Works of the Carnegie-Illinois Steel Corporation.

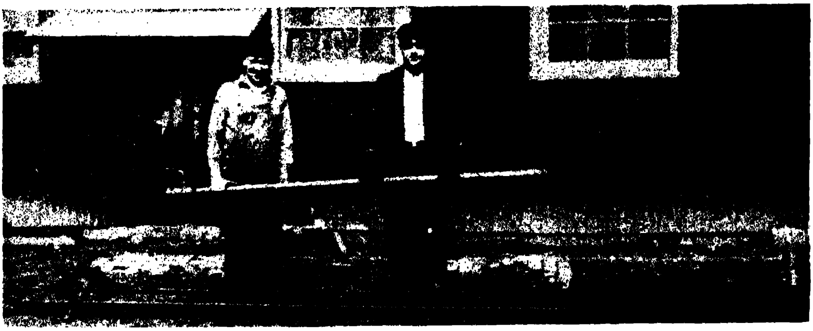

FIG. 3. Collins-Oseland tube (held by the men), and water-cooled dissolving-tube pyrometer (on the ground), as used in Pencoyd experiments in 1936.

As originally described,[3] and as used at Pencoyd in 1936, the Collins-Oseland tube consisted of a six-foot length of two-inch steel pipe, closed at one end with a heavy glass window and provided at its other end with a steel tip having a central orifice ½ to ¾ inch in diameter. A side opening connected the pipe with a source of air pressure. See Fig. 2 for a diagram of the tube, and Fig. 3 for its appearance as used in the tests at Pencoyd.

With air pressure on so that air is passing freely through the tube, the heavy tip end with the small orifice is inserted through a door wicket and submerged in the liquid iron or steel. A reading is then taken with an optical pyrometer sighted through the glass window on the bright spot outlined by the orifice in the tip. Readings must be made quickly before the pipe becomes hot enough to bend and before the tip begins to melt into the bath.

Although the observer sees only a bright disk of light, the reading is actually being made on the inner surface of a bubble or cavity in the liquid metal as seen through the orifice in the tip and maintained by the jet of air. This cavity is not a "blackbody," *i.e.*, a perfect radiator, because one side of it is cold, and the optical pyrometer readings must therefore be corrected. An emissivity of 0.61 had been roughly determined at Gary, based on comparisons with optical pyrometer readings, taken during tapping and teeming of the steel, but this proved to give temperatures that were too high.

Improvement of the Tube Method

The Collins-Oseland tube method as just described was found to yield quite self-consistent readings in the hands of an experienced observer. Its manual application in regular plant practice, however, is very difficult from a mechanical standpoint. It requires the services of two men, one to hold the pipe in position while the other takes readings with the optical pyrometer, and the observer is under some nervous strain to obtain a reading quickly. The pyrometer reader has to locate the small orifice, align it properly with the filament of the optical pyrometer, and make a blend in ten to fifteen seconds. Because of the air jet bubbling into the liquid bath, the tube is rarely steady and the customary make of optical pyrometer found in plant use is not sufficiently rapid to make an accurate reading in the available time. Finally, the method is open to the very serious objection that it is subjective and no automatic record can be made of the reading.

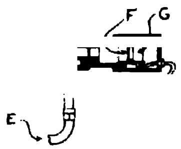

FIG. 4. Diagram of sighting-tube of photoelectric open-tube bath pyrometer. (Drawing adapted from U. S. Patent 2,184,169.)

A. Replaceable steel tip.
B. Outer pipe.
C. Inner pipe.
D. Diaphragms.
E. Hose connection for air supply.
F. Protective glass.
G. Photoelectric cell.

We therefore undertook to make the method automatic by using a photoelectric recording pyrometer in place of the optical pyrometer, and now have a satisfactory combination that is in routine use. The tube in its present form is shown in section in Fig. 4.

The photoelectric, automatically recording part of the pyrometer was first developed several years ago by the Research Laboratory to solve the problem of high-speed recording of solid steel surface temperatures.[4] Its adaptation to the bath pyrometer was easy in principle because the temperatures are higher and the intensity of the available light at its source is much greater than in the application to solid steel surfaces. Balanced against this is the fact that the distances are greater (six to eight feet), the visible area small, and the total amount of light energy consequently very minute.

The essential parts of the pyrometer are: (1) the inserted tube, (2) the photoelectric cell, (3) the automatic recording system. For the receiving cell we have utilized the self-generative or blocking-layer photoelectric cell in the form known as the Photronic cell. This cell delivers a current measured in microamperes, which is proportional to the intensity of light received on the cell surface. The current produced is nearly independent of external resistance and of the temperature of the cell. The cell is, however, subject to damage by temperatures above 120 °F and should therefore be guarded against overheating.

Known methods of amplifying and recording the current can be employed. For example, the cell current can be sent through a fixed resistance and the poten-

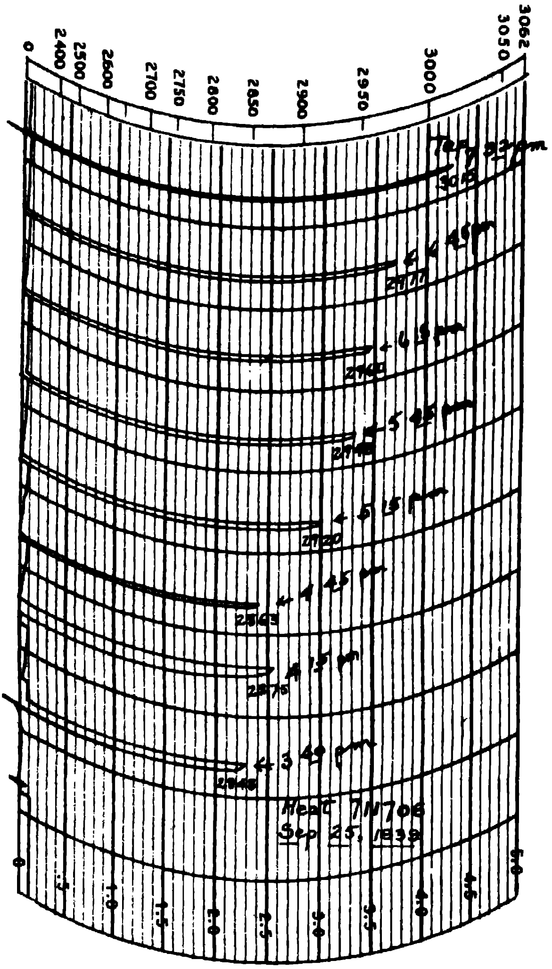

Fig. 5.

Example of a series of recorded temperatures of an open-hearth bath.

tial drop across the resistance can be recorded by an automatic potentiometer. Or the current can be amplified and made to operate a recording ammeter. In either case the scale of the recorder can be calibrated in terms of the temperature of the bath.

The Collins-Oseland tube itself, as used originally with an optical pyrometer, has had to be modified to adapt it to the use of a Photronic cell as the sensitive element in automatic reading and recording of liquid-steel temperatures. An internal tube has been added to support a set of diaphragms arranged to prevent wall reflections. This inner tube gives added stiffness to the entire unit in maintaining the proper alignment of the optical parts within the necessary limits (see Fig. 4).[5] It is impossible to prevent some distortion or bending of the outer tube and to some extent of the inner tube due to irregular thermal expansion from nonuniform heating, but a reasonable amount of distortion is permissible since only the small orifice in the tip and the last diaphragm nearest the Photronic cell determine the incident cone of light under proper conditions of operation.

The Photronic cell, which has a spectral sensitivity approximately corresponding to the visibility curve of the human eye, is well suited as a sensitive element in this application. Its response to radiant energy from a body below a dull red temperature is too minute to be detected with the arrangement used. This is of utmost importance since it eliminates errors due to radiation from the black hot interior walls of the tube; such radiation constitutes the major obstacle to the use of total-radiation receivers.

The output of electric current from the Photronic cell varies approximately as the twelfth power of the absolute temperature of the radiating source. This current-temperature relation is very useful for this application, since it condenses the unimportant portion of the temperature scale and greatly expands and magnifies the scale in the working range. In other words, on a temperature scale covering the range from absolute zero to 3100 °F, the last two hundred degrees from 2900 to 3100 °F extend over slightly more than one-half the entire width of the record.

Fig. 5 reproduces a series of bath-temperature readings made during a basic open-hearth heat. When this record was made we were still using the evenly divided milliampere chart of the recorder, special chart paper not yet having been prepared; but the scale drawn across the top illustrates the quality of rapid expansion of the scale, referred to above. It will be seen that a temperature of 3000 °F can be read with a precision of 5°. Readings can be reproduced within 10°. It is therefore possible to control the temperature of a bath of given composition—provided the temperature is uniform—to this precision. This does not mean that we know the actual temperature to any such degree of accuracy; absolute determinations must await further study and calibration.

The complete unit attains full-scale deflection in one second, and a satisfactory temperature determination requires but five seconds. In regular steel plant service, from eight to ten seconds constitutes standard practice in taking readings.

The all-steel tube in the hands of an experienced operator will last for more than a thousand readings and, barring an accident in handling, only the outer tube and tip need replacing. Readings at ten-minute intervals can be taken continuously with the same tube, and if desired two or three readings can be taken in rapid succession; but more time is then necessary for the tube to cool. Fig. 6 shows the pyrometer tube being introduced through the wicket of an open-hearth furnace door.

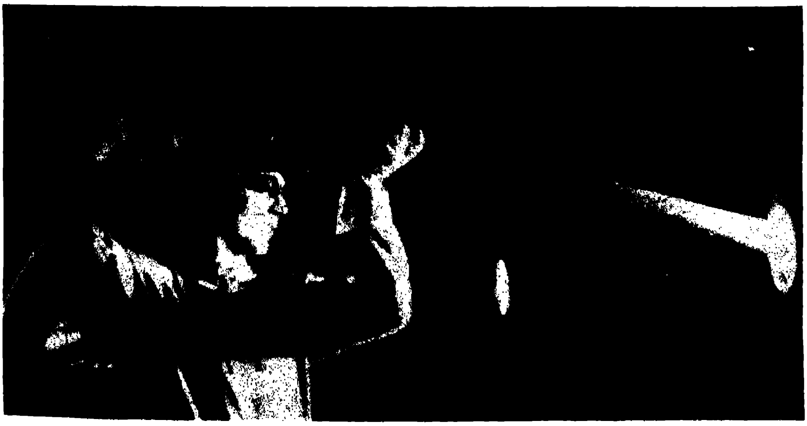

Fig. 6. Bath pyrometer in use.

Comparisons have been made with compressed nitrogen in the tube instead of air on ordinary steel baths below one per cent carbon during the last stages of the refining period. The nitrogen gave readings about 50° F lower than air and a trend was noted showing a very slight increase in temperature difference with increasing carbon content of the bath. In partial explanation of these effects it may be remarked that both air and nitrogen have a primary effect consisting of a cooling of the surface of the liquid metal. With air, this cooling would be balanced against the action of oxygen in reacting with the surface, brightening and heating it with the effect of making the apparent temperature higher.

Prior to furnace deoxidation or block, most open-hearth steels are fairly similar, with the exception of carbon content and the presence in some cases of the less easily oxidized alloying constituents nickel, molybdenum and copper; for this reason temperature readings during this period should be relatively comparable. However, the method has also been extensively used after furnace deoxidation, and after the addition of alloying constituents, on nearly every grade and type of alloy steel made in an open-hearth furnace, with consistent results and an undetectable effect from bath composition. The method is also being used in regular plant practice on electric furnaces, both in the furnace and in the ladle, on steels up to 14 per cent manganese, and in the acid open hearth on steels up to 2 per cent carbon, all with satisfactory results.

It is very improbable that there is no effect whatever from the bath composition, but rather that it is of such magnitude (less than 10 °F) that we are unable to detect it with our present unsatisfactory methods of comparison. It seems quite possible that the rapidly and continuously renewing inner surface of the bubble or cavity is swept out of the field of view before any chemical reaction can manifest itself, and as a result we have an apparent emissivity which will vary but slightly with variations in the small proportions of alloying constituents. The conditions are thus not comparable with those on the surface of a tapping or pouring stream.

The nature of the method has from the very beginning subjected it to the most critical and frequently skeptical scrutiny; and although it is proving its worth in regular plant use by eleven units in eight different plants, we have planned to conduct further tests and checks by means of an extensive thermocouple comparison under conditions of actual use, at the earliest possible moment.

Acknowledgments

We wish to acknowledge gratefully the assistance of various persons in the Research Laboratory and in the plants of the United States Steel Corporation who have had a part in these experiments, particularly Mr. Lewis Rumford II, who made the thermocouple measurements at Pencoyd; Messrs. Larsen and Shenk, who furnished advice on photoelectric pyrometry; Messrs. R. H. Cantrell, H. J. Chapin, Carl Oseland, J. W. Ready, Chester Siddall, H. B. Siddall, A. W. Thornton and J. D. Tyson, who took part in the Pencoyd comparisons; and Mr. J. W. Bain, who has assisted in the development of the pyrometer in its present operating form.

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A "Quick-Immersion" Technic for High-Temperature Measurements on Fluids

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I. Introduction

The best two instruments yet developed for high-temperature measurement are the platinum thermocouple and the optical pyrometer, the latter being used under blackbody conditions. In its application to fluids, each of these instruments normally involves the use of a refractory tube, which serves either as a sheath for the couple or a radiator for the pyrometer, and their success depends largely on the properties of such tubes. It is, of course, essential that adequate protection should be afforded to the couple and the required radiation conditions fulfilled for the pyrometer; and in addition, if routine measurements are to be attempted, that the tube be capable of repeated use or be replaceable at small cost.

The prevailing tendency, not only in relation to fluids, has been to increase the thickness of the tube and general massiveness of the apparatus, according as the temperature to be measured has become higher. In the case of liquid steel, at any rate, this procedure has not made possible the taking of routine measurements in the furnace. The reasons for this are that the tubes are costly and fail to withstand repeated immersion owing to the action of slag; that, with a heavy sheath, a thermocouple is likely to be contaminated to a greater extent because of the increased length of couple required to overcome end effect, and the increased time of exposure to high temperature arising from the necessity of preheating the sheath to avoid fracture; that thick-walled tubes are likely to give off fumes tending to obscure the field of the optical pyrometer.

In order to circumvent these difficulties the authors (Schofield and Grace, 1939) have recently developed a so-called "quick-immersion" technic which has enabled liquid-steel temperatures to be readily measured by a platinum couple up to the highest limit required, namely 1700 °C. According to this method the couple, lightly sheathed in silica, is plunged into liquid steel in such a way that a reading can be obtained in a few seconds and the couple withdrawn intact. The wastage of material and depreciation of the couple on each insertion have been rendered unimportant.

We give below a brief description of the method and of the parallel method, partly developed for the optical pyrometer, as well as a discussion of possible extensions of the technic, in the hope that they may find other industrial applications.

II. A Quick-immersion Thermocouple for Liquid Steel

The maximum speed of response of a thermocouple in a molten metal is no doubt given by immersing the bare thermocouple wires in the metal. This plan is sometimes used at moderate temperatures and its application to steel was considered in a former report (Schofield, 1937) and is briefly referred to in Section III.

The method was not pursued in this case because adequate speed was obtained with a lightly sheathed couple which seemed likely to be simpler in operation. The type of mounting used for a couple, consisting of wires having a normal diameter of 0.5 mm, is shown in Fig. 1. The response time of such an arrangement obviously depends on the material and thickness of the sheath, the diameter of the wire and the length of bare wire directly exposed to radiation from the sheath. The choice of the sheath material was restricted to silica by the conditions that it must be able to withstand sudden immersion in the steel, afford adequate protection to the couple, and not be too costly. It is true that silica is noticeably soft at the temperatures involved (1600-1700 °C), and that in the presence of reducing gases it is likely to cause contamination of platinum; but neither of these effects is such as to cause trouble during the very short immersion required to obtain a reading. In fact, a single sheath will generally allow 10 or more immersions in clean steel (*i.e.*, without a coating of slag) without depreciation of the couple, though the sheath may become bent or flattened during the process.

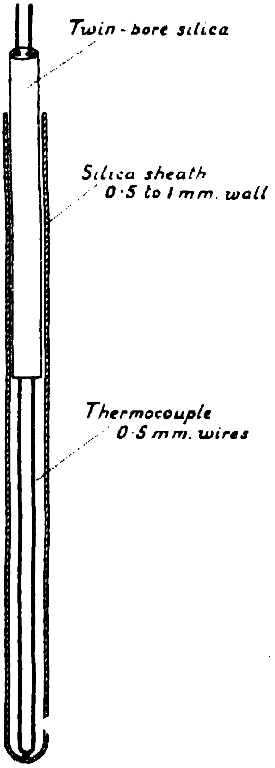


FIG. 1.

Mounting of thermocouple.

The quickest response for the type of mounting shown in Fig. 1 was obtained with a thermocouple having 0.3-mm wires and a silica sheath of 0.5-mm wall, and was of the order of 3 or 4 seconds, while the slowest response was 15 seconds, given by a 0.5-mm couple in a sheath of 2-mm wall. This thickness was found to be advisable when measuring temperatures in the launder stream, between the furnace and the ladle, owing to the thrust due to the moving metal.

The main difficulties in applying a thermocouple mounted as in Fig. 1 to the measurement of steel temperatures in a furnace arise from the comparative inaccessibility of the steel and the presence of slag, with its destructive effect on refractory materials brought into contact with it. The apparatus designed to meet these points is of the following description:

A 12- or 14-ft length of 1¼-inch pipe with a right-angle bend is cased in diatomite blocks as indicated in Figs. 2 or 3. These blocks, though they flux below 1100 °C, merely glaze on the surface during the 30 seconds or so for which they have to remain in the furnace, and their insulating power is such that after withdrawal from the furnace the pipe will only have risen by a few degrees in temperature. The pipe is inserted in the furnace either by the special trolley (Fig. 2) or by means of the regular furnace charger which picks up the adaptor DC (Fig. 3) on which the pipe is mounted. The pipe is then inclined until the vertical member dips into the steel through the slag. The end block of diatomite which has thus to come into contact with slag and steel is of a "heavy" grade, which was found to have the property of withstanding a number of immersions so that it provides, without undue chilling of the steel, a solid support for the thermocouple assembly which projects from it. This assembly was exactly as in Fig. 1, and it fitted into a metal end-piece screwed to the pipe and was held in the hole in the end block by a packing of asbestos wool. The thermocouple wires extended to the top of the vertical pipe and had surplus lengths wound on two insulated bobbins at this point. Connection was there made through compensating leads to the external indicator. Thus only a short length of couple is required, a feature rendered pos-

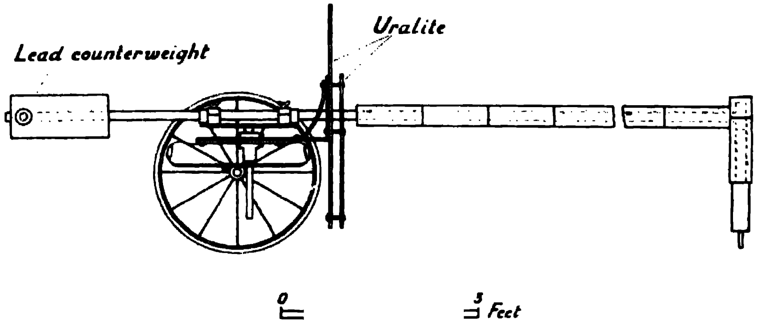


Fig. 2. Apparatus mounted on trolley.

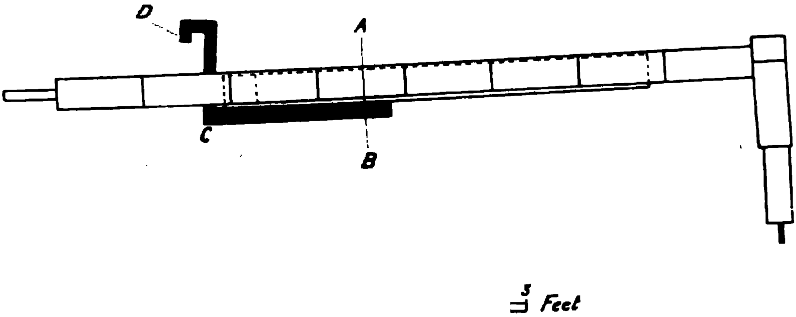
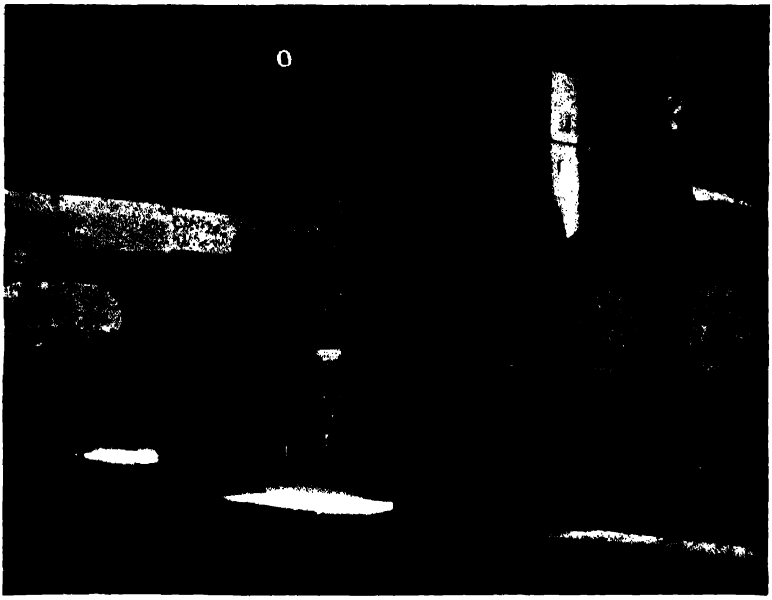


Fig. 3. Apparatus mounted on special adapter for furnace charger.



Courtesy English Steel Corporation, Ltd.

FIG. 4. Two couples mounted side by side ready for insertion into furnace. Note the effects of previous insertion: acid slag on lowest blocks, glaze on upper blocks.

sible by the fact, already mentioned, of the small temperature rise occurring in the diatomite-covered pipe.

On insertion of the thermocouple into the steel a reading is quickly obtained, and on its withdrawal the protecting silica sheath acquires a coating of slag which generally renders it unsound on cooling. The sheath, costing some 25 cents, must therefore be replaced after each insertion, a process which in general takes only a few minutes. The couple itself, in the absence of accident, will be intact and will undergo no depreciation for at least 12 and possibly many more insertions. When it is considered that contamination has occurred, the full emf can be restored to

Courtesy English Steel Corporation, Ltd.

FIG. 5. Apparatus being used in ladle.

the couple by cutting off an inch or two from the hot end, remaking the junction, and pulling the wires down from the bobbins to make up for the amount cut off.

The procedure indicated above has been applied to open-hearth and electric furnaces, both of the acid and basic types. With an acid slag, the end block of diatomite will pick up some slag on each insertion, and this may have to be broken off occasionally; whereas with a basic slag, corrosion is likely to occur which can, however, be minimized by a preliminary coating of alumina wash on the block. The life of an end block is from 6 to 12 insertions, and it can be readily replaced. Its cost is about 10 cents. As a measure of precaution, the authors adopted the plan of protecting the silica sheath with an outer sheath of thin steel. It is thought that the latter remains intact on its passage through the slag, but melts immediately in contact with the molten steel and thus prevents the silica sheath from coming into contact with the slag during insertion. It is, however, by no means certain that this precaution is essential. Fig. 4 shows two couples as described above ready for insertion in an open-hearth furnace. The effects on the diatomite blocks of previous insertion should be noted.

Courtesy English Steel Corporation, Ltd.

FIG. 6. Apparatus being used in launder stream.

For other particulars, such as full constructional details, tests relating to contamination, the best type of indicator to be used, and results obtained on actual furnaces, the authors refer to the 1939 report already mentioned.

The apparatus described above can be used in simplified forms for measuring the temperature of steel at several stages after it has left the furnace. Thus in the ladle, slag being present, the special end block must still be used, but the other diatomite blocks can be dispensed with and the mounting generally simplified. Such an apparatus in use on a 30-ton ladle is shown in Fig. 5. It will be noted that no auxiliary gear was used for making the insertion, though this might be necessary with a larger ladle. In the launder stream, in the trough, if one is used between the ladle and the mould, and in the mould, the apparatus may be still further simplified owing to the absence of slag. Thus in the first two cases it suffices to have a pipe with a right-angle bend into the end of which a silica sheath is fixed. The apparatus can be quite light and be readily operated by hand without any auxiliary gear. An example of the apparatus in operation on the launder stream is shown in Fig. 6. In this case it is advisable to immerse the silica with its end pointing downstream and inclined at a moderate angle to the surface, and, as already mentioned, to employ a sheath of wall thicker than the normal, *e.g.*, 2 mm in place of 0.7 mm.

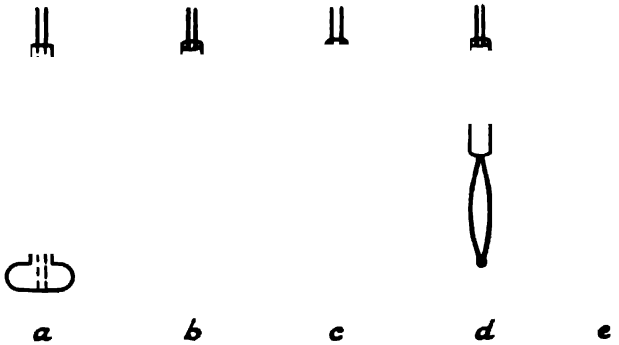


FIG. 7. Arrangements for mounting thermocouples with bare junctions.

III. Possible Modifications of the Quick-immersion Thermocouple

The devices described above, though designed primarily for liquid steel, could no doubt be adapted with slight modification to other molten metals at temperatures not higher than those encountered in steel practice, for example, to copper in a reverberatory furnace. On the other hand, the properties of non-metallic fluids differ so greatly from those of steel and other metals as to call for considerable alteration. Thus the low thermal conductivities of such fluids, as for example optical glass, would perhaps mean too much lag in a sheathed couple, and the insertion of a refractory sheath might in itself be objectionable on the ground of contamination of the fluid or disturbance of its physical state. Further, non-metals generally differ from metals in that their attack on platinum couples will be relatively slow and unimportant. For these reasons a bare, or partly bare, thermocouple might be particularly advantageous for non-metallic fluids.

In Fig. 7 are shown various possible arrangements for such a couple; *a* is a diagrammatic representation of an apparatus designed by Rogers (1917) for liquid steel. The essential features of this apparatus are that the wires of the couple are embedded in a block of refractory material, and have their ends exposed on the lower surface of the block so that on insertion into the steel a circuit is completed between the wires. The disadvantages of the arrangement would seem to be the lag due to the close contact of the wires with the refractory block, the need for preheating, and the difficulty of renewing the thermocouple end when it becomes contaminated.

Arrangements *b* and *c* were used by the authors in their preliminary work on steel. It will be seen that the wires project from a twin-bore silica tube, being joined together in the one case and unjoined in the other. The latter arrangement is of course unsuitable for a non-conducting fluid. The response time in molten steel of the assembly *c* is probably a small fraction of a second, whereas that of *b* may be several seconds according to the mass of material at the junction of the wires. The ends of the wires can readily be replaced by pushing out fresh wire from the twin bores. On the other hand, it is necessary to maintain a stream of gas down the bores to prevent them from being clogged by the fluid, and this may be a serious inconvenience.

Arrangements *d* and *e* are specially suitable for fluids which can be relied on not to corrode or contaminate a platinum couple during a short immersion. In *d*, the wires must be sufficiently stout to stand insertion in the fluid without deflection of the loop of wire. The wires are sealed through a twin-bore tube of silica or other material, and the seal must be broken from time to time to replace the depreciated end of the couple. In arrangement *e*, the only materials brought into contact with the fluid are the stiff wire or rod of platinum and the light thermocouple wires attached to it. For the latter, wires as thin as 0.1 mm could be used, and their attachment to the platinum support could be by twisting, or welding. In fixing the couple the junction should be well away from the support, as shown in *e*, to insure a quick response. The use of very thin wire would enable frequent replacements to be made at low cost and so reduce the risk of contamination.

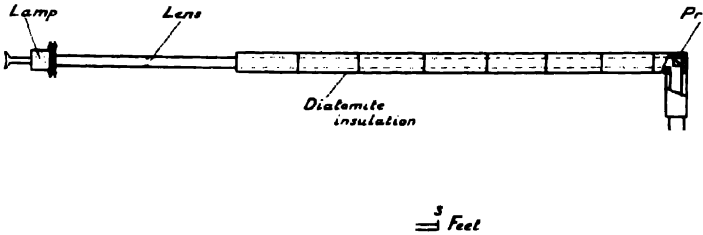


FIG. 8. Apparatus arranged for use with optical pyrometer.

IV. A Quick-immersion Technic for Radiation Pyrometers

Radiation pyrometers, particularly of the optical type, have been applied to the measurement of steel temperatures in the furnace, mainly by two methods, *viz.*, the use of a closed-end sight tube kept immersed in the steel, and of a tube or other object first immersed in the steel and then withdrawn to serve as a "target" for the pyrometer. The tube or object so employed would have to be comparatively massive, and hence would probably be costly and be characterized by considerable lag. Further, in the case of a heavy-walled tube, fumes are likely to form and obscure the radiation; while in the case of a target, difficulty would arise if it should become coated by slag, which would affect both its temperature and emissivity.

The possibility of developing a quick-immersion technic for radiation pyrometers was therefore considered. Although the plan was not fully worked out, in view of the success obtained with the thermocouple, it is perhaps worthy of description here.

The plan will be understood by reference to Fig. 8. It will be seen that, in externals, the apparatus is similar to that used for the thermocouple (Figs. 2 or 3), and that the long tube for insertion into the furnace contains at its cold end the usual optical system of the disappearing filament pyrometer. On insertion of the sight tube into the steel, light from it is reflected by a prism or mirror in the position shown, and focused by the objective lens onto the plane of the lamp filament the brightness of which is adjusted to match it in the usual way. Arrangements have, of course, to be made for lining up the optical system, especially on account of the sag of the long tube with its load of diatomite insulation. For this purpose the prism, or mirror, was mounted on a block removable through the top end of the T-piece, forming the right-angle bend, and was provided with adjustments for bringing the object into view. At the other end of the system the lamp box and eyepiece, forming one unit, had to be provided with vertical and tilting movements. A flat plate was screwed to the end of the pipe; and, with a thick rubber washer intervening, the lamp box was clamped to this plate in such a way as to give the required movements.

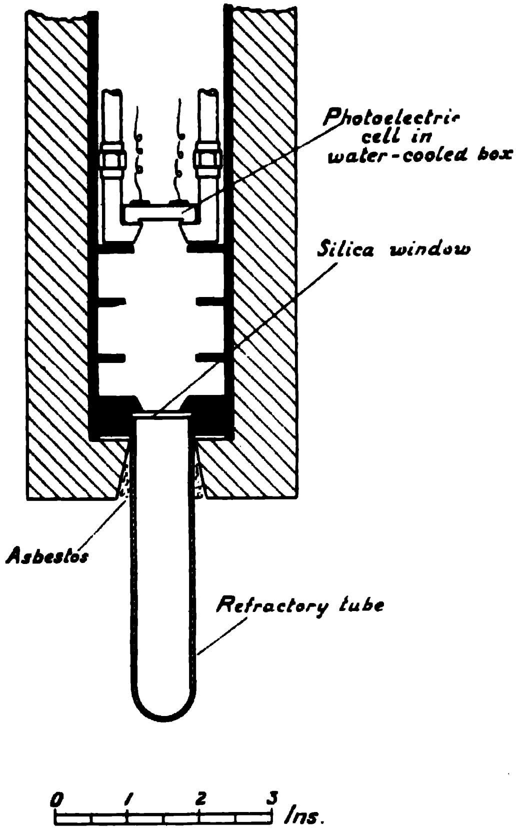


FIG. 9.

Apparatus arranged for use with photoelectric cell.

It was found that the assembly of the apparatus and lining-up of the parts could be accomplished in 15 minutes or so, and that, with a sight tube of ¼-inch bore, the extreme amount of vibration to be expected in the pipe did not displace the image to such an extent as to prevent satisfactory readings being taken.

The material to be used for the sight tube depends to some extent on the time taken to get a reading. By preheating the filament to about the right temperature, this time can be reduced to some 15 seconds. Even with so short an immersion there would be some risk of obtaining a false reading owing to the distortion or collapse of the tube if made of silica. The possibilities of silicon carbide as an alternative were therefore considered. It was found that tubes of this material withstood the shock of sudden immersion in the steel when made in similar dimensions to the silica tubes used for thermocouples, *e.g.*, 5-mm bore and 0.5-mm wall or 7-mm bore and 0.8-mm wall. Such tubes are rapidly attacked by molten steel, but this difficulty was overcome by a thin coating of alumina wash. A valuable feature of these tubes is that, since they withstand sudden heating, even in the oxy-coal-gas flame, it is easy to free them from moisture or other constituent likely to give rise to fumes on insertion into the furnace.

Further particulars with regard to the suggested use of the optical pyrometer on a quick-immersion plan will be found in the report already referred to (Schofield, 1937).

The main disadvantage of using an optical pyrometer as described above arises from the necessity of cleaning certain parts affecting the calibration, particularly the prism or mirror, and the trouble of lining up the system after each cleaning.

As an alternative to the optical pyrometer, other radiation instruments might be used. Thus a photoelectric cell might be mounted as shown in Fig. 9, and placed in the upright end tube of Figs. 2, 3 or 8. It will be noted in Fig. 9, that the diaphragm system is such as to limit the field of view of the cell to the walls of the radiating tube where they are in contact with the molten metal. Since photoelectric cells generally have large temperature coefficients, it would be advisable to insure that the cell is at a known temperature at each insertion. For this reason the cell is shown in Fig. 9 surrounded by a water jacket, to be connected to a supply for some time before an immersion so as to reach a constant temperature. The supply could be disconnected before insertion into the furnace, since the quick response of the instrument would render the maintenance of the flow unnecessary during an observation.

Summary

A description is given of a so-called "quick-immersion" technic by which a platinum thermocouple is applied to the routine measurement, up to a maximum of 1700 °C, of the temperature of liquid steel in the furnace and elsewhere. The method consists essentially in lightly sheathing a couple in silica so that it can be plunged into liquid steel, give a reading in a few seconds, and be withdrawn intact. The use of a bare, or partly bare, thermocouple is briefly considered with a view to its application to other fluids, particularly non-metals.

A "quick-immersion" technic, partly developed for the optical pyrometer is also described and its possible extension to a photoelectric type of receiver is touched on.

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Pyrometry of Liquid Steels and Pig Irons

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Introduction

Twenty years ago, at the symposium on temperature measurement held by the American Institute of Mining and Metallurgical Engineers, the Dean of Pyrometry of that time, Dr. George K. Burgess, stated[1] with reference to the measurement of liquid steel temperatures: "Previous investigations have shown some of the difficulties to be overcome: mechanical, metallurgical and thermal in nature. The pyrometer itself is the least of these. The greatest is a refractory that has the requisite mechanical, chemical and thermal properties; it must be robust enough, when hot and cold, to withstand abuse; it must withstand the corrosive action of basic and acid slags, flames, hot gases and liquid steel; be non-porous and not give off fumes or water vapor when heated; it must not crack on sudden heating or cooling and must be able to withstand a temperature of nearly 1700 °C; and finally it must be capable of being manufactured into closed tubes of convenient size with a thickness of wall that is not too great, nor of too low thermal conductivity, to allow the interior to assume rapidly the temperature of the region into which it is thrust."

Dr. Burgess thus aptly stated the problem of temperature measurement, whether the method be optical or thermoelectric. He went on to recommend tentatively the use of graphite tips, which might be immersed in liquid steel so that optical pyrometer readings could be taken on their exterior surface immediately after their removal from the furnace. Also, a hollow graphite tip could be used and the optical pyrometer sighted down to the closed end of the tube during its immersion in liquid steel. He recognized and pointed out several defects in both of these methods.

The problem of liquid steel temperature measurement may still be divided into mechanical, metallurgical and thermal aspects. A fourth aspect, which was not mentioned by Dr. Burgess, may be termed the practical aspect. It is that the measurement must fit into, and not interfere with, ordinary plant routine.

This practical aspect of the problem is the one which has been found most impeditive by the active workers in this field, who have been striving to overcome the mechanical, metallurgical and thermal difficulties. Operators in the mills are concerned primarily with production and delivery. They will stand for no interference with their operations, regardless of what claims are made for the accuracy and general scientific utility of an apparatus. An instrument, to be accepted by the liquid iron and steel industries, must not only be of acknowledged accuracy but must be so constructed that the least possible number of man-hours (or man-minutes) is required for its operation. In many plants it must operate *continuously* with little attention. Installation and maintenance costs must be low.

Moreover, no pyrometer of any sort will ever be successful in liquid iron and steel applications unless it reveals sufficient metallurgical information to show the operators why they should use it for control purposes. No instrument is ever going to be accepted until it reduces to a science some of the "mysteries" in the art of steel-making. The development of the platinum-platinrhodium thermocouple by Le Chatelier reduced the mysteries in the art of heat-treatment to a science—a science of many ramifications, as it is today. This is exactly what is needed in the liquid iron and steel industries. The useful qualitative information that we now have must be placed on a quantitative basis through the use of measuring instruments. Formerly, the few instruments used in the melting shops were not taken seriously and their results were used only as a guide by the melter. If the instrument showed an abnormally low or high temperature, the melter disregarded the reading entirely and tapped the heat on his own judgment. And he was not to blame when—as was the case until recent years—his "guesstimate" of temperature was more reliable than the readings of unsuitable instruments. By unsuitable instruments are meant those which operators opposed on practical grounds (interference with plant routine as explained above) and also the following categories:

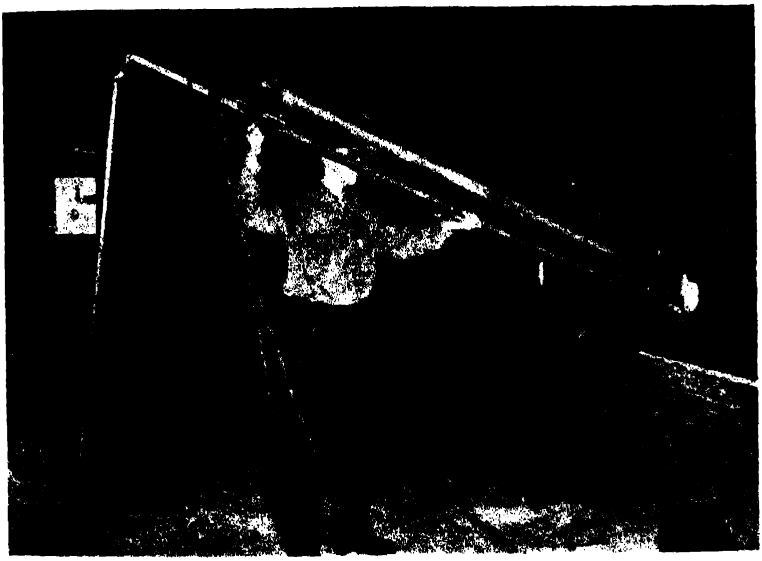

FIG. 1. A portable C-SiC thermocouple for open-hearth bath temperatures.

(1) Instruments inherently unsuitable because their primary measuring elements wore out too quickly when exposed to liquid metal and slag. (Examples, rare-metal couples in various combinations of inner and outer "protecting" tubes which had to be renewed so frequently that the cost in man-hours was prohibitive—in addition to the "interference" objection.)

(2) Instruments inherently unsuitable because of the too-early occurrence of sources of error invisible to the eye of the operator. (Example, the rapid contamination of thermoelements by gases passing through protecting tubes from the start or—at best—long before the tubes showed visible signs of becoming unsuitable.)

(3) Instruments theoretically suitable for measuring liquid iron and steel temperatures (some of them successful in the laboratory), but in practice unsuitable because they became "instruments of torture" in actual use in proximity to emergent streams of liquid metal or to melting furnaces, large ladles, etc. (This has been a serious obstacle to the accumulation of metallurgically useful data, such as

temperature-time curves and other data requiring periods of observation too long for human endurance.)

(4) Instruments theoretically suitable but too delicate, too complicated, etc. (Even where the electrical or electronic "instrument end" of the system met no objection, any system with a relatively fragile assembly in contact with molten metal and slag was obviously unsuitable.)

The melter was not to blame, then, for mistrusting instruments; and quantitative data were unobtainable without instruments. But all this is changing by reason of the successful development of thermoelectric pyrometers which comply with all requirements outlined above. In all these new pyrometric systems the primary element is the graphite *vs.* silicon carbide type of thermocouple which was first announced[2] in 1933 and which in the ensuing three or four years was satisfactorily developed for uniform manufacture and practical use. (No detailed description of the construction and characteristics of the C-SiC thermocouple will be included because they have been described elsewhere.[2,3,4] However, for those unfamiliar with it, Figs. 1 and 2 are photographs showing the general appearance; Fig. 3 is a sectional drawing showing a typical assembly; and Fig. 4 compares the temperature-emf characteristic of the C-SiC couple with those of others.)

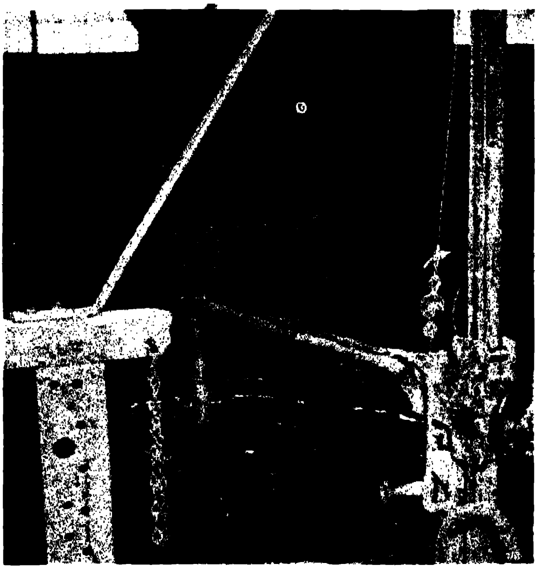

FIG. 2. A ladle-type C-SiC thermocouple in use.

In the last five years, quantitative data obtained through the use of the C-SiC thermocouple have revealed a fast-growing amount of metallurgical information, of which the following is an incomplete list:

(1) The solubility of carbon in certain types of pig iron.[5]

(2) The effect of the above on the surface quality of large castings such as ingot molds.[6]

(3) Cooling characteristics of 100-ton "submarine" or car type ladles transporting liquid pig iron.[7]

(4) Temperature variations in a 1000-ton Bessemer mixer (see Fig. 5) and the probable cause of certain variations in blowing such iron in the converter.[8]

(5) The determination of the critical freezing ranges of a great variety of liquid steels.[9]

(6) The development of the principle of "temperature head" and the application of this principle in the teeming of steel ingots.[10]

(7) The effect of temperature on the rate of carbon elimination in the acid open-hearth furnace.[11]

Liquid Steel

An attempt will be made to answer the challenge stated by Dr. Burgess by describing and discussing the service record of one of the steel ladle C-SiC thermocouples which has been in constant operation since June, 1936.

This unit (Fig. 2) has been used in the determination of temperatures in the ladle of an acid open-hearth shop for more than 2000 heats since its installation. It may be seen from the figure that the couple is suspended on a long, horizontal water-cooled arm and that it can be moved both horizontally and vertically. It can be swung around over the ladle and pushed down through 10″ to 12″ of liquid slag and into some 8″ to 10″ of liquid steel.

A ladle thermocouple has to be of rugged construction to withstand abuse in production. This unit is inserted by the pit men, and the indicating potentiometer is operated by the first helpers. The pit men service the thermocouple by maintaining the refractory wash.

The thermocouple has a replaceable graphite tip 15″ long and 1¾″ in diameter. After this has worn down to about 1⅜″ in diameter it is taken out of service.

In the application under consideration the tip is usually taken out of service after 60 to 70 heats, although in one case a tip lasted for a total of 162 heats. Throughout the three-year service the average tip life in this unit has been approximately 60 heats. As explained in previous articles [2,3,4] the life of a tip depends upon the particular service required. Refractory washes are supplied with the couple and their composition depends upon the application. In some new applications the life of the tip is much less than that mentioned above, but after a little development work the composition originally supplied is changed and the tip life is increased.

No breakage due to thermal shock has ever occurred in any installation since the original development of the C-SiC thermocouple. The tip may be plunged cold into steel well above 3000 °F, without breakage of any part of the unit.

Readings with the unit being described require about three minutes, since the thermal conductivities of both silicon carbide and graphite are high. Preheating is desirable, so as not to hold up the ladle longer than this period, in case of a "cold heat." In this plant, the length of ladle holding time is determined by the measured temperatures.

The time required for the measuring junction of the SiC-C thermocouple to reach the temperature of the liquid steel in which it is immersed is not longer than that required by the protected thermocouples commonly used in high-temperature service. It is actually less than that required by thermocouples with double or triple protection. One of the reasons for the speed of operation of the C-SiC thermocouple is that the graphite tube itself is one of the thermoelements. (See Fig. 3.)

No significant change in the calibration of C-SiC thermocouples has ever been encountered, even after long use at high temperatures. Several units have been recalibrated after as many as 100 immersions in liquid steel without showing any

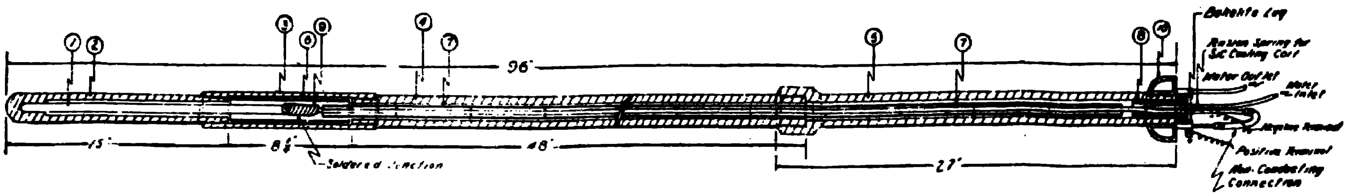

FIG. 3. Sectional view of C-SiC thermocouple assembly. 1—Silicon carbide rod. 2—Graphite tip. 3—Graphite sleeve. 4—Graphite main section. 5—Graphite head nipple. 6—Fused silica insulator (1⅜"×1⅛"×8"). 7—Fused silica insulators (23/32"×⅝"×5"). 8—Porcelain insulator. 9—Copper cooling coil for SiC. 10—Copper cooling coil for graphite.

changes of more than ±5° F. In one laboratory experiment, for a period of two weeks a thermocouple was heated twice daily to 3600 ° F and held at that temperature for one hour each time. Recalibration after this two-week treatment also showed no changes greater than ±5 °F.

Resuming now the discussion of the practical ladle unit: The life record of one silicon carbide thermoelement is shown in Fig. 6. This SiC rod was used in the measurement of 185 forty-ton heats of steel, or a total of 7400 tons. Each point represents the temperature of a forty-ton ladle of steel. The points are arranged in chronological order. It may be seen that there is no gradual increase or decrease in the temperatures with the length of service. The temperatures ranged between 2800 and 2900 °F both at the beginning of the run and at the end, with an occasional heat above or below this range. These 185 points were taken from the furnace log book of the plant in which this unit is installed.

The fluctuations seem to be quite regular and probably represent heats melted by different furnace operators. Some operators regularly work their furnace hotter than do others, as many companies have learned.

According to the company records, these 185 heats of steel, whose temperatures were measured by this one SiC rod, varied considerably in analysis. Most of them were medium-carbon, low-alloy steels. They are listed below, together with their various grades, their carbon contents and their "apparent freezing points" which were determined by the method discussed previously[9]:

Number of Heats	Steel Grade S.A.E. Number	Carbon Content (%)	Apparent Freezing Point (°F)	
34	1000	0.20–0.60	2700–2760	
20	2300	0.30–0.50	2660–2720	Depends on
4	3100	0.40–0.50	2670–2710	
41	4100	0.14–0.60	2700–2760	Carbon
56	4300	0.40–0.60	2670–2720	
4	4600	0.20	2700	Content
26	6100	0.40–0.50	2620–2690	

This information is given to indicate the variety of steels into which the unit was inserted during the life of only one SiC rod.

The parts used during the life of this SiC rod were the rod itself, and three tips. This would indicate an operating expenditure of about 0.4 cent per gross ton of steel. Over a period of three years, however, the operating expense of this thermocouple has been under 0.2 cent per ton, and by paying off the initial cost over a three-year period the total expense has been less than 0.3 cent per ton.

Liquid Pig Iron

Pig iron for open-hearth furnaces is tapped from the blast furnace into a runner or trough, down which it flows to ladles, which transport it to the mixer furnaces. The mixer is a large holding vessel which may contain from a few hundred to a few thousand tons of liquid iron at a time depending upon the demand in the particular plant. The furnace is heated only slightly so as to keep the refractories in the upper part of the furnace hot. No attempt is made to heat the pig iron to any particular temperature.

Whenever an open hearth requires pig iron, a small ladle is taken from the mixer. Before the introduction of the C-SiC couple, no data were available concerning the variations in temperature of this iron from the time it leaves the blast furnace until it enters the open-hearth furnace.

Some operators have always maintained that the temperature of the liquid pig iron has a decided effect upon the quality of the resultant steel. This point was discussed at great length at the joint meeting of the blast furnace and open hearth operators last spring.[12]

That the carbon content of pig iron changes rapidly with temperature is evident from the iron-carbon phase diagram. Also other elements, particularly sulfur, silicon and manganese, are known to change considerably in pig iron, depending upon the temperature. This point was also discussed at length at the 1939 joint meeting.

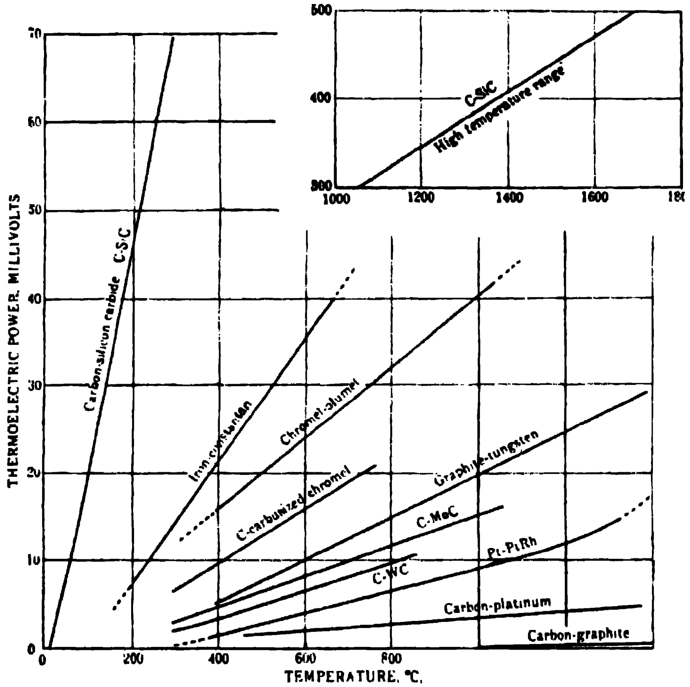

FIG. 4. Comparison of temperature-emf relation of C-SiC thermocouple with those of other industrially useful thermocouples. (Courtesy A.I.M.M.E.)

One of the first steps in the study of these composition changes with temperature was taken by one of the larger steel companies about one year ago. They installed a C-SiC thermocouple for taking temperatures of the pig iron as it leaves the blast furnace. The thermocouple tip is inserted in the liquid metal about ten feet from the tap hole of the furnace where there is a deep well in the trough or runner. The C-SiC thermocouple assembly is 22 feet long and is suspended over the point of insertion. When the runner has filled with liquid metal just after the furnace has been tapped, the thermocouple is lowered into the liquid iron to a depth of as much as 12". The depth of metal at this point is about 18", and if the thermocouple is lowered much below this point the temperature will be lower because of the cooling effect of the refractory runner. Also if the couple is inserted to only a few inches, a slightly lower temperature will be indicated because of radiation losses.

At the instant that the tip of the thermocouple touches the liquid metal, a limit switch starts the chart of the potentiometer recorder and in less than two minutes after immersion the thermocouple attains the temperature of the flowing metal. Usually the metal runs from the furnace for half an hour or 45 minutes and the thermocouple is left in the bath until about the last five minutes of the cast. When it is removed, the limit switch stops the chart of the recorder, and the thermocouple is again ready for use, except for inspecting the condition of the tip and, possibly, brushing with a refractory wash.

One of the chief advantages of this unit is of course the fact that no special operators are required. Furnace helpers can raise and lower the couple and the temperatures are recorded automatically.

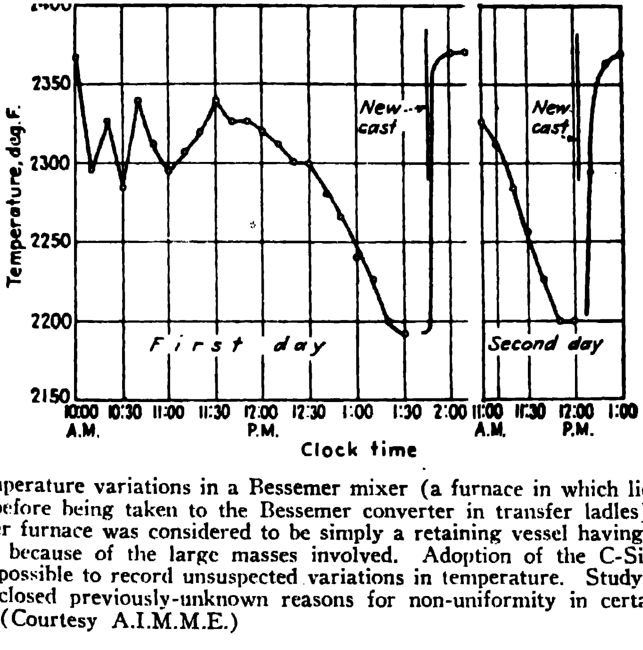

FIG. 5. Temperature variations in a Bessemer mixer (a furnace in which liquid pig iron is held before being taken to the Bessemer converter in transfer ladles). Formerly the mixer furnace was considered to be simply a retaining vessel having no effect on the iron because of the large masses involved. Adoption of the C-SiC pyrometer made it possible to record unsuspected variations in temperature. Study of such records disclosed previously-unknown reasons for non-uniformity in certain Bessemer steels.. (Courtesy A.I.M.M.E.)

A number of interesting data—of practical value—have been determined through the use of this unit. One of these is that tap-hole difficulties are recorded. If the stream is small, because of a clogged tap hole, the runner refractories will chill the metal and the length of the cast will be increased as will be the time of recorded temperatures. This may be contrasted with a cast which has a full run, in which case the temperatures are high for the shorter period.

It is understood from the men close to this installation that the temperatures being recorded can be correlated with the analysis of the metal, particularly with respect to silicon and sulfur.

The life of the tips in this installation has been increased so that as many as 37 casts have been obtained with one tip. At an average of 30 minutes per cast this amounts to about 18 hours of service. Also this installation is not preheated prior to immersion, and this is an indication of the ability of the unit to withstand thermal shock.

Over a seven-month period, the expense of operating this unit has been less

than 0.25 cent per ton, and by paying off the original installation cost in one year and including the maintenance, the cost of operation is about 0.75 cent per ton.

Reproducibility

The above has been a discussion dealing with some of the more practical aspects of the C-SiC thermocouple. There are other matters which should also be discussed, one of which is the reproducibility of the thermoelements. This topic has only received brief mentions in previous articles on the C-SiC couple; therefore an attempt will be made to treat it adequately here.

Under present operating conditions the *graphite elements* of the thermocouple are extruded to size and shape, after which they are thoroughly graphitized. In this condition, the graphite is reproducible within the required small limits of error.

Until recently the *silicon carbide elements* were ordered under broad specifications. All rods were calibrated, and if they did not fall within the desired limits they were not used as thermoelements. Recently, however, it has been found that rods of desired calibrations may be obtained on the basis of resistivity, which in turn is a function of their manufacturing procedure.

Rods are now being obtained which are more nearly within the desired range and are therefore reproducible. As previously stated, the thermoelectric power of the C-SiC thermocouple is extremely high, being of the order of 300 microvolts per °C. (About half a volt at ladle or bath temperatures.) It will be recalled also that the relation between temperature and emf is linear:

$$(T-C)\ ^\circ\mathrm{F}=dT/dE\ (\text{millivolts})$$

or,

$$(T-50)\ ^\circ\mathrm{F}=6.00E\ (\text{mv})$$

More than 350 thermocouples have been calibrated to date and about 80% have held within 1% of this formula. By specifying on the basis of resistivity as mentioned above, it is expected that more than 95% will fall within the desired ±1%.

The thermocouples may depart from this standard formula in two ways. Either the value of dT/dE may differ from 6.00, or the value of C may differ from 50.

All potentiometers used with this thermocouple now have a slide-wire calibration corresponding to this formula, and are furnished with an auxiliary resistance coil at the base of the slide wire for raising or lowering the setting of the slide wire at will. The auxiliary resistance is graduated and the user is furnished with the proper setting for each thermoelement.

In case the value of C is greater or less than 50, a simple adjustment of this coil will adjust the potentiometer to the calibration of the thermocouple. This adjustment rarely involves a change of more than 2 or 3 millivolts or 12 to 18 °F.

Whenever the slope of the calibration curve is different from 6.00, however, another procedure is followed. Let us assume that the thermocouple has an undesirable slope, 6.06 instead of 6.00, and that the application involves the use of the thermocouple at an average temperature of 2750 °F. At this temperature the standard couple would indicate 450 millivolts, whereas this couple would indicate $(2750-50)/6.06$ or 445.54 millivolts. On the other hand, at 450 millivolts according to the potentiometer this couple should indicate 2777 °F. By adjusting the auxiliary rheostat this couple can be made to conform to the potentiometer chart or 2750 °F.

Admittedly this is the only point at which the two curves agree but the residual errors are less than 3° between 2450° and 3050°.

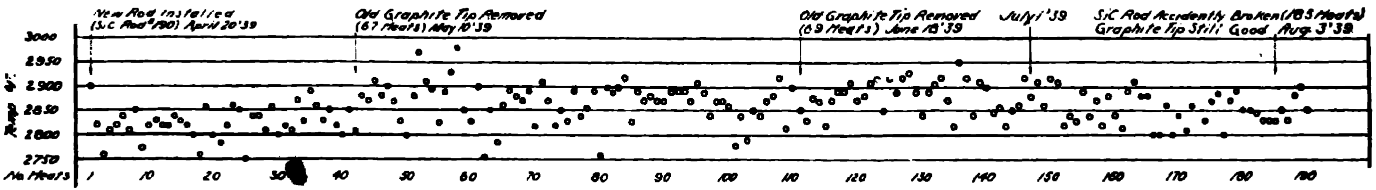

FIG. 6. The life record of one silicon carbide thermoelement. See text for interpretation.

Inasmuch as the range between 2450 and 3050 °F covers the steel-making range, the potentiometers used in this work cover a limited range also; consequently by this means even thermocouples which have a slope different from that desired can be made to conform with the recorders or indicators within the limits of error just reviewed.

Another point which might be mentioned with reference to reproducibility is brought out in Fig. 6. The last five points on the curve have reference to the new SiC rod that was installed after the old one had been broken and replaced. It can be seen that the new rod continued on recording the same range of temperatures as the one which was taken out of service.

Appendix

Note on the Properties of the SiC supplied for the Rods employed in Fitterer Thermocouples.

Thermal Conductivity

150 °C	0.0032	g. cal/°C/cm^2/sec
1200 °C	0.027	do.

Resistivity

Room temperature	0.54	ohm/cm^2/cm
760 °C	0.0936	do.
1500 °C	0.36	do.

Discussion

C. B. Post, Metallurgical Department, Carpenter Steel Co., Reading, Pa.: Experience in basic electric furnace practice would lead one to suspect that an emissivity correction different from 0.4 should be used by open-hearth producers on reading tapping temperatures if a correction of 0.4 is used by steel producers who tap fully killed steels. This is the experience of melters who have to judge the temperature of both "wild" and "killed" steels.

There is a type of basic electric furnace steel of low alloy and medium carbon content which is kept in an oxidizing condition until about an hour before tap. The deoxidizers are added after the slag has partially turned reducing, and the heat is tapped. Temperature of the metal in the oxidizing period will appear very high, that is, 1600-1610 °C; but after the deoxidizers are added to give a killed steel, the temperature will be judged and read by the optical pyrometer when tapping is to be in the neighborhood of 1570-1580 °C.

These facts indicate that the emissivity of wild steel is closer to that of a blackbody than is the emissivity of killed steel. Furthermore, it is a well-known fact that basic electric furnace practice, using small ladles and small ingot molds appropriate to 11 tons, yields relatively hot steels; and, as previously brought out at the meeting, a high temperature for killed low-carbon basic electric steel at tap is about 1600-1610 °C, using the emissivity correction of 0.4.

I believe that melters who have melted steel in both open-hearth and basic electric furnaces would agree that if killed steel which taps at 1600-1610 degrees should be raised to 1640-1660 degrees (as is frequently reported for tapping temperatures in the open hearth) no ordinary nozzle or stopper rod would be able to hold the metal in the ladle. The appearance of a furnace not specially adapted for high-temperature work (such as the furnaces used to make stainless steel from chrome ore) after being subjected to temperatures of 1640-1660 °C, would be an interesting sight.

Open-hearth and basic electric furnace tapping temperatures are approximately the same; an apparent difference arises because the open-hearth tapping temperatures are obtained on wild metal (emissivity coefficient expected to be greater than 0.4), whereas the basic electric tapping temperatures are obtained on killed steels (emissivity almost 0.4 as determined by the National Bureau of Standards in 1920).

Appropriate technical committees of metallurgical societies might consider this question, and if it is decided that the problem is real, might attempt to find this difference in emissivity constants so that steelworks metallurgists can discuss temperature effects referred to a standard scale. The thermocouples of Fitterer, if they have the accuracy claimed, or the type of "quick immersion" thermocouple developed by the British Iron and Steel Institute, would serve admirably for the purpose of standardization.

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Some New Measurements of the Melting Point of Iron and of Ferrous Oxide

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In experimental work on molten iron and its alloys, no other secondary reference temperature is as useful as the melting point of iron itself. Yet there has been considerable uncertainty as to what this temperature actually is. The data were carefully reviewed by Cleaves and Thompson[1] in their recent work "The Metal, Iron." They show that all the data, when corrected to a palladium point of 1555 °C, lie in the range 1527 to 1538 °C, and recommend 1535° as the best value. The degree of uncertainty associated with this choice is evidenced by their further statement that the two researches which seem to have been executed with the greatest care are those which gave the two extremes of the temperature range. The causes of the discrepancies are by no means clear, but one very possible source of low results lies in the presence of elements which are not ordinarily determined in the analysis of iron and steel. Oxygen in the form of iron oxide is frequently present in carefully prepared vacuum-melted iron, and it is sufficiently soluble in liquid iron (0.21 per cent oxygen) to depress the freezing point about 10°.

An opportunity to redetermine the melting point by an independent method and to study the effect of oxygen was seen in an apparatus which was used in the study of equilibrium[2] at high temperatures in the reaction $FeO+H_2=Fe+H_2O$. The metal used in this study was carbonyl iron obtained as sheet 1.2 mm thick. The common impurities were present only in traces, except nickel, of which there was 0.031 per cent. To remove carbon and oxygen the iron was annealed in hydrogen in a previously annealed iron tube at 1200°C for 100 hours, after which it contained 0.002 per cent oxygen. The annealing treatment was extended for an additional 100 hours, after which the oxygen content was less than .001 per cent and carbon less than 0.005 per cent.

Strips of this material were cold-rolled to 0.27 mm thickness and specimens were sheared to the desired size and cleaned in hot hydrochloric acid before use.

The furnace arrangement is shown in Fig. 1. The heating element was a silicon carbide (Globar) tube 5 cm I. D. and 55 cm long. Power was supplied by a motor generator controlled by a variable resistance in the field circuit. By hand regulation it was possible to maintain temperatures constant within ±2° up to 1600 °C, or to raise the temperature at any desired rate.

Inside the heating element was placed a slightly longer tube of impervious alumina (Alfrax 2 B). The platinum-platinum-10% rhodium thermocouple was mounted inside a small porcelain tube (McDanel) which was inserted from the top. Cemented to this tube were two alumina discs which acted as radiation shields. For the same purpose the lower part of the tube was filled with a refractory insulating brick (K-30) the topmost piece of which extended well into the zone of uniform temperature. Between brick and disc was a distance of some 15 cm within which no temperature differences could be detected by movement of the thermocouple. As further evidence of uniformity, it was found in observations through the top of the furnace, using blue furnace glasses, that objects within this zone could not be distinguished. Specimens of iron 5 cm long used in melting-point determinations showed incipient melting uniformity over their entire length.

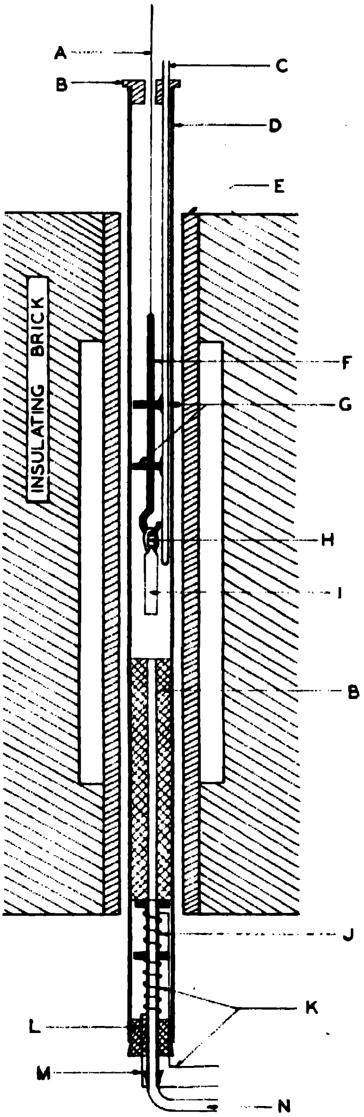

Fig. 1. Furnace.
A, nickel suspension wire; B, insulating brick; C, thermocouple tube; D, impervious alumina tube; E, silicon carbide tubular element; F, Alundum rod; G, Alundum discs; H, beryllia ring; I, specimen; J, porcelain tube; K, resistance wires; L, rubber stopper; M, wax joint; N, hydrogen inlet.

The specimen (*I* in Fig. 1) was suspended from a small ring, *H*, made of beryllium oxide. This was hung on the end of an Alundum rod, *F*, whose lower end was ground into a hook and whose upper end extended into the colder parts of the furnace where it was suspended by a nickel wire, *A*, from a balance above. The rod was free to move through holes in the radiation shields, *G*. The melting point was observed by raising the temperature at a rate of 1 degree in 2 or 3 minutes and noting the temperature at which a loss of weight occurred. Fig. 2 is a photograph of one specimen used in determining the melting point of the oxide and of the remains of two metallic specimens after melting-point determinations.

Temperatures were measured on a platinum-platinum-10% rhodium thermocouple encased in a porcelain tube. The same couple was used for all determinations, but the protection tube was changed occasionally, and two of these were broken to determine whether the surface darkening had penetrated through the sheath. In both cases the darkening was found to be superficial; the inner portion of the tube and the two-hole insulator were clean and white at all times. The couple was calibrated before use at the melting points of copper, nickel and palladium (1555°). During and after the equilibrium study it was rechecked at these points; and finally, after the melting-point determinations, it was again checked by the method used for iron, at the melting point (in air) of a specially purified palladium kindly furnished to us by Dr. Edward Wichers of the National Bureau of Standards. In all the comparisons the couple agreed with the standard tables within 1 °C.

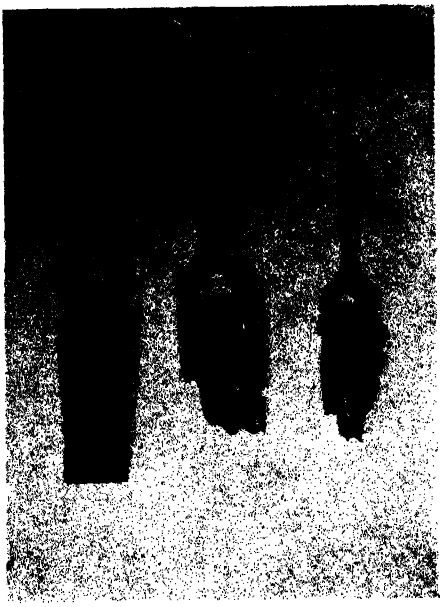

FIG. 2.

Specimens used in determination of melting points of oxide and metal.

The oxidizing or reducing nature of the atmosphere in the furnace was at all times under control. High-grade water-pumped hydrogen was first passed over platinized asbestos at 500 °C, then through distilled water in a saturator which was maintained at a controlled temperature. The use of dry hydrogen was avoided because of its reducing action on most refractories. In no case was the water-vapor pressure sufficiently high to cause the formation of an oxide phase on the specimen. The limiting steam-hydrogen ratio corresponding to the formation of the free oxide was determined, and a slightly lower ratio was used in two determinations of the melting point, Expts. 3 and 4 of Table 1. In these two experiments

Table 1. Melting Point of Iron.

Exp. No.	P_{H_2O}/P_{H_2}	M.P. (°C)
1	.034	1534.0
2	.037	1534.3
3	.674	1524.4
4	.666	1524.4

the iron specimen was therefore correspondingly slightly below saturation with respect to the oxide. In two other experiments, 1 and 2, the ratio was quite low, so that the proportion of oxygen imparted to the metal was very small.

Up to saturation, the equilibrium oxygen content of the iron is directly proportional to the ratio[3] P_{H_2O}/P_{H_2}, and it is therefore possible, without an actual determination of the oxygen present, to extrapolate on the one hand to zero oxygen and on the other to saturation. The extrapolation which is shown in Fig. 3 yields the interesting result that the melting point of oxygen-free iron is 1535°, and that of oxygen-saturated iron 1524 °C. These results agree with the average value recommended by Cleaves and Thompson[1] and with the melting point of oxidized iron reported by Bowen and Schairer.[4]

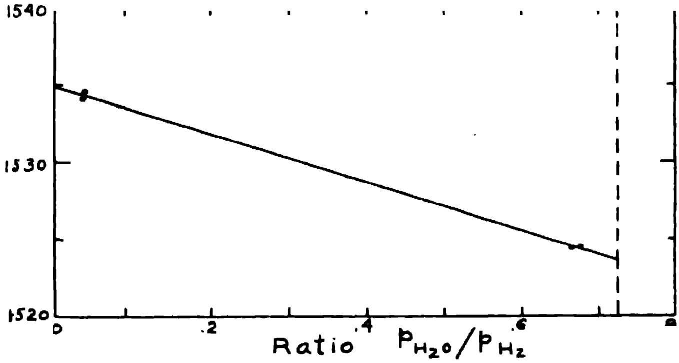

FIG. 3. Effect of oxidation on the melting point of iron.

A similar method was used to determine the melting point of the oxide phase formed by gaseous oxidation of the metal. This temperature was reported as 1370° by Tritton and Hanson[5] and 1380 ± 5° by Bowen and Schairer.[4] The metal specimen was held at 1360° in a very weakly oxidizing atmosphere until about 2 or 3 grams of solid oxide were formed. The steam-hydrogen ratio was adjusted to approximately the equilibrium value and the temperature was slowly increased. With a rate of rise of 1° per minute melting occurred at 1370°. This was evidenced by a sudden loss of weight of about 1 gram of oxide. The molten oxide is very fluid and no appreciable time lag for the formation of the drop would be anticipated. In a second run the temperature was increased more slowly, about 1° in 3 minutes, and this time melting occurred at 1369°. This represents the melting point of the solid solution "wüstite" in equilibrium with solid iron. The composition is not that of a simple compound FeO but, according to Jette and Foote,[6] is 76.8 per cent iron. The composition of the liquid was determined by analysis of the material adhering to the iron after the melting point observation. This was found to contain 77.0 per cent iron.

Summary

The melting point of an oxygen-free iron containing 0.031 per cent nickel as its only significant impurity was found to be 1535 °C. The same iron, when saturated with oxygen, melted at 1524°. The melting point of ferrous oxide (wüstite) in equilibrium with iron was 1369 °C.

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Pyrometry in Connection with Creep Tests

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The measurement of the creep rate in materials at elevated temperatures is a problem demanding the most careful control of the temperature in order to secure consistent results. As the rate of creep of a material can often double with a temperature change of as little as 12° Fahrenheit, it is easily realized that temperature errors are very serious in this type of work. It is the purpose of this paper to describe briefly some of the methods that we have found useful in providing a uniform temperature in the creep test laboratory at the Massachusetts Institute of Technology.

Thermocouples and their Calibration

A great deal has been written concerning the use and calibration of thermocouples, so that I need touch on this phase of the subject only briefly. Our general procedure is to calibrate with great care a master platinum-platinum-rhodium thermocouple at the freezing points of pure tin, zinc, aluminum and copper. These materials are obtained from the Bureau of Standards with certified freezing points. We then plot a standard curve for this type of couple, and using this curve as a basis, a deviation curve is obtained for our particular couple. We find in most cases that the deviations are comparatively small, so that interpolation between the four calibration points can be easily accomplished. We also have a working standard platinum-platinum-rhodium thermocouple which is compared two or three times a year with our master standard. This working standard is used for calibrating the individual couples used on the creep test specimens, and it is our general practice to calibrate a couple before and after each test. This comparison is made in a special constant-temperature furnace with both couples carefully mounted close together in a heavy metal block, and the cold junctions of both are kept in ice.

Using this method it is possible to determine the temperatures to ±0.3 °F with the platinum couples, but with the Chromel couples ±1 °F is as good as can be expected because of their change in calibration. This change from the normal curve is shown quite clearly in the following table:

Table 1.

Couple	Weld and Anneal	After 1st 1000-hr test	After another 1000-hr test
1	1.4 °F	2.3 °F	2.1 °F
2	0.0	1.6	0.7
3	0.0	0.6	2.1
4	1.0	1.8	1.3
5	0.0	0.8	1.2

All values are positive.

A point of importance in measuring the temperature in creep tests is the attachment of the thermocouple to the specimen itself. Many methods for carrying this out have been recommended, such as hammering the bead into a hole, putting it into a socket in one end of the specimen, and tying it onto the surface. We have found that the last method is most satisfactory because the couple is not deformed or cold-worked during attachment, and therefore has no calibration change. It should be remembered that, if we have a specimen with an even temperature from end to end, there can be no longitudinal flow along the specimen, and therefore no heat is transferred from the wall of the furnace to the specimen. Under these conditions a thermocouple anywhere in the space between the specimen and the furnace wall would measure the true temperature. For this reason a perfect contact of the thermocouple and the surface specimen is not necessary. It is only in the shorter types of specimen that we are apt to have heat interchange between the furnace wall and specimen over the gage length.

Uniformity of Temperature throughout the Specimen

The temperature distribution in the specimen is more satisfactory when longer specimens are used, which is somewhat contrary to our earlier conception. The temperature distribution is usually measured by tying a number of couples onto the surface of the specimen in various positions. For ordinary work three couples on a ten-inch specimen are quite satisfactory. Because of the variation in thermal resistance of the threaded joints, it is necessary to have controllable end coils on the furnace to supply just the same amount of heat as is conducted out of the furnace by the specimen. It will be found that each specimen requires a different adjustment of these end coils, and it is quite futile to attempt to determine the distribution of a given furnace with a dummy specimen and then expect the same distribution on the test specimen. The following table brings this out very clearly:

Table 2.

Condition	Temp. diff. between top and bottom: 2" spec. (°F)			
	(a)	(b)	(c)	(d)
1st spec. as run	+1.2	+0.3	+1.2	+1.3
2nd spec. before loading	+20.8	−7.3	−2.8	−15.7
2nd spec. before loading approx. adjust.	−0.6	−3.7	−1.4	−3.5
2nd spec. load same adjust. as above	−9.7	−7.1	−16.7	−4.7

In designing the winding on a furnace it is desirable to have a long, uniform coil in the center and concentrated end coils with separate control. These should be controlled, if possible, by a rheostat or transformer having a zero temperature coefficient, as we find some difficulty in maintaining our distribution because of drafts or cold air striking the rheostats. It is also helpful to have a massive furnace tube to iron out the small temperature irregularities. In a well-designed furnace it is not out of the question to maintain a temperature over the section of ±1 °F, and we seldom exceed this limit in our testing.

With most of the modern types of extensometer it is necessary to have one or more windows in the side of the furnace so that the reference marks can be seen from the outside. These windows should be kept as small as possible and the winding should be arranged to give a few extra turns around the window to make up for the heat lost by radiation and conduction at this point. Even under the best conditions, however, there is apt to be a cold spot opposite the window, and this may give difficulty if the window is in the center of the gage length of a short specimen, as the cold spot will then amount to an appreciable portion of the specimen itself. With ten-inch specimens, however, the cooling by the window is a much smaller proportion of the whole and would generally give no trouble. In the case of short specimens, if the windows can be placed outside of the gage length at the ends, no trouble will be encountered.

These windows must, of course, be tightly covered with glass to prevent drafts and turbulent motion, which prevents accurate reading with the telescope. The glass should be so arranged that it can be quickly removed and replaced for cleaning, as fumes from the furnace tend to gradually obscure it.

Uniformity of Temperature with Time

A great many methods have been described for controlling the temperature of small furnaces. The method that we are using in our laboratory is one originally developed in England, and depends on the expansion of the furnace tube itself to control the temperature. A complete description of our apparatus has been published and need not be repeated here.[1] This expansion is magnified about 100 times by a simple lever, and contacts at the end of the lever cut in or out approximately 10 per cent of the power supplied to the furnace. No relays are necessary and the reliability of the apparatus is surprisingly good. At the present time the limiting factor in our control is the room temperature, which can be held to better than ±1 °F with our present controllers; and for this reason we find variations in temperature of the specimen of approximately ±0.5 °F. On the other hand, if we make a run for a short period of time in which the room temperature is constant, we find that the furnace control will produce a variation not over one-tenth of this, as shown in Fig. 1. We consider that this control is remarkably good for such an extremely simple apparatus.

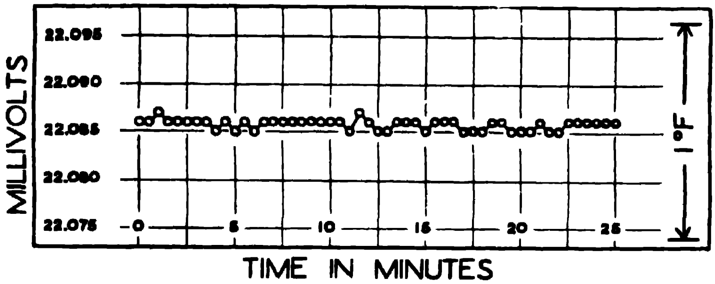

FIG. 1.

Discussion

W. G. Benz and R. F. Miller, United States Steel Corporation, Research Laboratory, Kearny, New Jersey: The method for the calibration of thermocouples which Prof. Norton describes is used at the Research Laboratory of the United States Steel Corporation at Kearny and, in our experience, seems to be the best method available.

In addition to Table 1, the following figures may be offered to show the reasonable stability of Chromel-Alumel couples in a relatively inert atmosphere at 1000 °F.

	July 30, 1937	September 6, 1938	June 19, 1939
No. 1.	− 1.3 °F	− 1.0 °F	− 0.2 °F
No. 2.	− 1.4 °F	− 1.1 °F	− 0.7 °F

In the description of the attachment of couples to the specimen, Prof. Norton mentions that deforming or cold-working may result when thermocouples fit into holes drilled through the center of the threaded ends of the specimen. At Kearny the temperature inside the specimen, as measured by a couple fitted into this socket arrangement, agrees with a couple tied to the side of the specimen. The thermocouple slips in readily and no deformation of the couple has been encountered.

In our apparatus, five couples are used for the measurement of temperature uniformity on the 2" gage length. The design of the specimen, its pullrods, and extensometer system permit the use of a dummy specimen for checking temperature uniformity. This has been proved by checking the temperature uniformity of the furnace with more than one dummy specimen. The dummy is identical with a specimen.

Instead of a massive furnace tube, a nickel sleeve which fits inside the furnace winding over the gage length decreases the small variations to ±1 °F.

It has been our experience at Kearny that a small window (¼"×½") does not produce a cold spot, as evidenced by a couple tied to the specimen in back of the window. However, the window must be far enough away from the specimen. That is, the furnace must be of fairly large radius, 3 to 4 inches, and the winding must be wound around the window.

As Prof. Norton mentions, control of room temperature has been found to be extremely important. The control apparatus which Prof. Norton uses appears to give very accurate results.

J. J. Kanter, Research Metallurgist, Crane Co., Chicago, Ill.: We are unable to add anything of a very pertinent nature to what you have already said in your paper. Our experience with the expansion temperature controller which you discuss has been limited to a modification of your own type used in connection with a relaxation tester, upon which it gave very creditable results. We were not, however, able to attain the close limits of regulation, which you have experienced in your own laboratories. This may be attributable to lack of as much experience with this type of device as you have had.

Our experience with the obtaining of uniformity throughout the gage length of test specimens confirms in general the conclusions brought out in your paper. Each creep test must be carefully balanced up with respect to temperature before and throughout the test, the temperature being balanced at a number of points both within and on the surface of the specimen. In general, one might say that as far as the tested section of metal is concerned, the heating conditions surrounding it must be such as to minimize heat transfer as much as possible. Bearing this principle in mind, one will encounter the greatest success in accurately designed creep furnaces for precise temperature control and maintenance.

In order to attain precision of control, it may interest you to know that we have recently installed in our new creep testing laboratory a complete air-conditioning system which maintains a laboratory temperature of 80 °F at all times. In addition to an increased precision of temperature control, greater comfort is provided for the creep testing technicians, which contributes greatly to the psychological influence over precision in creep testing.

P. G. McVetty, Mechanics Dept., Westinghouse Electric & Manufacturing Co., Pittsburgh, Pa.: I am thoroughly in agreement with the statement as to the importance of close temperature control. Our experience indicates that creep rates double for a temperature change of as little as 6 °F. It appears to me that all laboratories will have to come to the close control which you have attained. It is a serious problem to hold our large furnaces within such close limits, but our efforts are resulting in gradual improvement.

Your care in calibrating couples leaves little chance for doubt as to the accuracy of your temperature measurements. I was rather surprised at the small change in reading after 1000 and 2000 hours of test (Table 1). This depends on the test temperature which is not given. We have had greater effects of aging, and I understand that Battelle also has had trouble. Before starting a test we peen 21 couples into small holes in the steel central core of our furnace. These are arranged in three groups of seven, 120° apart, located at the top, center and bottom of the 20-inch gage length, center of the top and bottom windings, and just below the top and above the bottom porcelain insulating blocks. These are replaced at the end of every run to minimize aging effects. We use them to adjust temperatures before inserting the test specimens; as a continuous check on temperature uniformity; and to operate the temperature controls. We are unable to calibrate these couples after use, because it is impossible to remove them without damage. The original calibration may be changed somewhat by cold work during the peening operation, but we have not found any serious errors from this source.

While we take complete readings of core temperature at least twice a week for comparison, these observations are not used in determining the specimen temperature. For this purpose we use five couples which are inserted through the wall of the furnace at 5-inch intervals along the 20-inch gage length. These are held against the surface of the specimen by external springs. Readings are taken after temperature equilibrium has been reached and then the couples are removed. The time of exposure of these couples to high temperature is relatively short, so that aging effects are minimized. They can be calibrated as often as desired without disturbing the creep tests. Some of our present tests have run over 12,000 hours, and we would expect appreciable aging effects at 1000 °F if the couples were tied to the specimens.

Is it possible to hold the room temperature within ±1 °F over long periods of time, say one year? We have automatic controls on our heating system and ventilating fan with hand-operated steam radiators for severe cold weather, and louvers in the doors for hot weather. Our room varies from 85 to 100 °F in the hottest summer weather. We have considered a cooling system, but it would require better heat insulating in the walls. Also, our three furnaces dissipate about 12 kw, and a fairly large system is required. We have been collecting data to support a request for an appropriation for air conditioning but we cannot yet prove that such an installation would insure better control within the furnaces. We have tentatively set 85 °F as the best year-around temperature for the room. This is based on the assumption that it is cheaper to hold the average up to this value in winter than it is to cool below this level in summer.

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Temperature Measurement of Red Brass (85-5-5-5) During Melting and Casting

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Introduction

The Non-Ferrous Ingot Metal Institute, upon the recommendation of the American Society for Testing Materials, has sponsored a study of the physical properties of cast copper-base alloys at the National Bureau of Standards since 1930. This has, of course, necessitated careful consideration of the foundry variables affecting the properties of the alloys.

Early in the investigation a study was made of the effect of pouring temperature upon the physical properties of the alloy made from virgin metal and from remelted metal.[1] Later, the effects of impurities on the physical properties of the alloy, made from remelted metal, were determined. The effects of small additions of sulfur, iron, aluminum and antimony, as individual impurities in the alloy, have been determined.[2,3] Studies of the effect of other elements, commonly found as impurities in this alloy, are in progress.

Roeser and Fairchild in 1926,[4] in their paper "Pyrometry of Molten Brass," reported the results of a survey of 24 representative non-ferrous foundries and discussed the essential principles of thermoelectric pyrometry and the many types of industrial pyrometers in use at that time. Following that survey, many improvements were made by pyrometer manufacturers. Most foundries now recognize that an accurate knowledge of melting temperature and of pouring temperature assists greatly in the production of good castings. The present paper summarizes the work being conducted at the National Bureau of Standards in the investigation sponsored by the Non-Ferrous Ingot Metal Institute. It includes an outline of the methods considered as possible means for measuring temperatures for this project, the reasons for selecting the method that has been used, and, in addition, discussion of some of the results that have been obtained.

Importance of Temperature Control

There is probably no other single factor in the foundry that has a greater influence upon the quality of the finished material than the proper pouring temperature. It would be convenient if there were only one optimum pouring temperature for each alloy and for all types of casting; but in order to obtain sound castings in foundry practice, the optimum pouring temperature for any alloy depends upon such factors as design, thickness of casting, quality of metal, method of gating, type of mold and condition of mold material, *i. e.*, dry or green sand, cement or plaster mold.

It may be said that metal is generally poured at the lowest temperature at which the mold can be properly filled. If the metal is cast too cold, "misruns" may be expected to result. If it is cast too hot, the metal may retain oxides or other impurities which at the proper pouring temperature would have been removed in the slag. Their non-removal results in "dirty" castings. Then, too, metal cast too hot has a tendency to cause a sintering of the sand of the mold to the casting, and necessitates additional work to produce the desired smooth finish.

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* Research Associate representing the Non-Ferrous Ingot Metal Institute.

The maximum temperature to which the metal is subjected in the furnace and the "soaking" at high temperature are also important. It is well known that molten metal has a tendency to absorb gases, and that the higher the temperature the greater the amount of gas absorbed. Consequently, overheating or prolonged "soaking" of the molten metal at a high temperature favors the absorption of greater amounts of gas. Upon cooling, these gases are liberated, generally while the metal is in the solidification temperature range, and thereby produce porous, brittle castings. By experience, foundrymen have learned to avoid heating the metal to excessively high temperatures or permitting it to "soak" in the furnace unduly long after it is ready to cast. For many alloys, especially for those of the red brass group, recommended practice is conceded to be as follows. Melt the alloy as rapidly as possible and, with suitable protection from the gases of combustion, heat the molten metal to the temperature which experience has shown to be satisfactory for the work at hand, and no higher; then, after the necessary slagging operation, cast at the proper pouring temperature as determined with a pyrometer.

The type of furnace used generally governs the type of equipment best fitted for temperature measurements in the furnace. For commercial foundries either the bare-metal thermocouples or pyrometers of the type described by Grubb, Marshall and Nass [5] are satisfactory for control of pouring temperature because of the rapid temperature readings they permit. By use either of a portable instrument, which may be readily carried through the plant, or of a fixed type, whereby the molten metal is "routed" to the pyrometer station and then poured according to a schedule determined by the accurately measured temperature, industry has long since learned that temperature measurements during melting and casting are essential for the production of good material.

Methods of Temperature Measurement in Casting Red Brass

Preliminary to the foundry program itself a number of methods utilizing thermocouples for temperature measurement were considered. These included:

(1) Noble-metal wire thermocouples (platinum to platinum-rhodium)
(2) Base-metal thermocouples
  (a) Bare-wire thermocouples
    (a′) Fork type
    (b′) Welded tip
  (b) Enclosed thermocouple with the hot junction protected by a metallic tube [5]
  (c) Enclosed thermocouple, protected by a glazed porcelain tube which, in turn, is enclosed in a closed-end graphite tube.[6]

A comparison of noble- and base-metal thermocouples showed that temperatures up to 1320 °C (2400 °F) could be measured to ±5 °C with base-metal couples; hence, the more expensive platinum to platinum-rhodium couple was used only for occasional checking of the base-metal thermocouples. It was recognized that both the fork type and the welded-tip type of bare-wire thermocouples, as ordinarily used, record the temperature of only the surface of the molten metal. However, if the bare wires are immersed in the molten metal to a sufficient depth, *e. g.*, 8 inches, and, after a reading of the temperature of the surface of the molten metal has been obtained, the wires are partially withdrawn until only approximately 4 inches of wire are immersed, and a "quick" reading is taken, it is possible to obtain an indication of the temperature of the metal in the pot. Without a doubt the method does permit the quickest reading and, with proper attention to details, is being successfully used with both the fork-type and the welded-tip type of bare-wire thermocouples, because for many purposes the temperature measured in this way is sufficiently characteristic of the temperature of the metal being poured. However, important factors that must not be overlooked when using this method are the inconvenience and incorrect readings which may result from (1) slag occlusions on the wire or tip; (2) rapid oxidation and consequent pitting of the wire submerged in the molten metal; (3) the absorption of the two wires in the metal at different rates; and (4) the fluctuation of the needle while taking readings. Although it is recognized that there are temperature gradients within any ladle of metal handled in a foundry, it is felt that a temperature measured at some point below the surface will be more characteristic of the metal being poured than the temperature of the surface. Attempts to insulate the wires by the use of porcelain or asbestos insulation, and thereby to obtain temperature measurements of the metal in the crucible by this method, proved unsuccessful and so the method was discarded for this investigation.

Consideration next was given to the enclosed thermocouple developed by Grubb, Marshall and Nass,[5] in which a protective closed-end metal tube is used. Advantages claimed for this type are that, since the mass of the protection tube is small and the amount of thermal insulation between the hot or "measuring" junction and the molten metal is small, it is possible to measure quickly and accurately the temperature in the interior of the metal. This method is only slightly less rapid than the use of the bare-metal thermocouple. However, for the requirements of this investigation, of which a major part was a study of the effect of small quantities of added impurities, chiefly metallic, on the physical properties of the alloy, it was deemed imperative that a non-metallic protection tube be used. This eliminated the possibility of metallic contamination of the molten metal from the protection tube itself. Accordingly, a thermocouple as shown in Fig. 1 was assembled, as follows: The thermoelectric pyrometer consists of a thermocouple, extension leads, and a potentiometer for measuring the emf generated. The thermocouple consists of a Chromel wire and an Alumel wire, both B. & S. No. 18 gage, welded together at one end to form the "measuring" junction or hot junction. These wires, separated by means of a two-hole porcelain insulator, are enclosed in a closed-end, glazed porcelain protection tube which is inserted in a closed-end graphite tube. The latter is immersed in the molten metal to an approximate depth of 8 inches, the precaution being taken always to keep the hot junction one inch from the bottom of the crucible. The free ends of the thermocouple wires are attached to extension leads, which terminate in an ice bath at 0 °C, so that the emf generated bears a fixed relation to the temperature of the hot junction. Copper wires are run from the ice bath to the potentiometer.

It is recognized that this method may not be sufficiently rapid for use in industrial work, but in this investigation, involving the preparation of a great number of heats in which the development of a "standard practice" was necessary in order to keep the number of variables at a minimum, it has served admirably for temperature measurements, both during the time of raising the temperature to the desired maximum while the crucible remains in the high-frequency induction furnace, and during the time of pouring. It has been found that approximately one minute is required to bring the thermocouple up to temperature, when the cold thermocouple is inserted in molten metal. When the temperature of the metal is changing, the temperature of the thermocouple will lag behind that of the metal, because of the heat capacity of the thermocouple and protection tubes. This is shown as thermometric lag, and is thoroughly discussed by Harper.[7] The temperature of the thermocouple protected and used as described here was found to lag only about 2 °C behind that of the metal when the temperature of the metal is changing by 25 °C per minute. As the maximum rate at which the temperature of the metal was changing during either melting or pouring was not greater than 25 °C per minute, the thermometric lag is considered insignificant.

FIG. 1. Thermocouple assembly used in measuring temperatures of molten red brass (85-5-5-5).

A. Thermocouple-handle enclosing extension leads;
B. Thermocouple junction with extension leads;
C. Chromel and Alumel thermocouple wires;
D. 2-Hole porcelain insulating tube;
E. Porcelain protection tube;
F. Graphite tube;
G. Split lock nut;
H. Pipe tee;
K. Insulating plate.

The outer graphite protection tube prevents any erosive action of the molten metal or slag on the inner porcelain protection tube. Furthermore, it reduces the thermal shock to which the porcelain tube is subjected when the device is lowered into the molten metal. It is advisable, however, to introduce the thermocouple gradually into the molten metal so as to minimize breakage of the porcelain tube by thermal shock.

Procedure of Pouring

A "standard practice" for melting and pouring red brass of the 85-5-5-5 composition was developed some years ago.[1] It provides that the molten metal be heated about 55 °C (100 °F) above the desired pouring temperature. The power of the induction furnace is then shut off, the crucible is removed from the furnace and placed in pouring position before the molds, and the metal, after it has cooled to the desired pouring temperature, is cast into test bar molds. As each mold is poured, a temperature reading is taken. To reduce the temperature drop of the metal in the crucible during the pouring interval, a double crucible with the intermediate space filled with chrome ore has been used. Even with such a crucible, however, a drop in temperature of 25 °C at a pouring temperature of 1230 °C is often observed during the time required for pouring 12 molds. Heats cast at 1065 °C show a drop during pouring of only 15 °C. On account of this drop in temperature during pouring, the practice has been followed of pouring the first test bar in each heat at a temperature of 10 °C above the nominal pouring temperature. The mean pouring temperature of each group of bars, *i. e.*, of each heat, is then a close approximation of the desired pouring temperature.

Effect of Pouring Temperature on Physical Properties of Red Brass

In the early part of this investigation this red brass alloy was cast into test bars at pouring temperatures of 1040 °C (1900 °F), 1095 °C (2000 °F), 1150 °C (2100 °F), 1205 °C (2200 °F), and 1260 °C (2300 °F). The effect of variation in pouring temperature was quite pronounced. Excellent physical properties were obtained on test bars cast at 1095 °C (2000 °F) and 1150 °C (2100 °F), indicating that metal cast in this range should be the most satisfactory. Although only small differences were noted in the physical properties of bars cast at lower temperatures, a marked inferiority in properties was observed for similar specimens, especially sand-cast test bars, poured at the higher temperatures of 1205 °C (2200 °F) and 1260 °C (2300 °F). Later in the investigation only three pouring temperatures were used, 1150 °C (2100 °F), which was the optimum pouring temperature for this alloy and these types of castings, 1065 °C (1950 °F) and 1230 °C (2250 °F), which were approximately equally distant below and above this optimum temperature, and may be considered as close to the limiting temperatures at which this alloy may be successfully poured commercially. It was expected that the latter temperatures would supply data on the properties of the alloy cast "on the cold side" and "on the hot side," respectively.

In the study of the effect of small percentages of individual impurities on the physical properties of the alloy, it was found that the effects of sulfur and iron were masked by those of pouring temperatures. In the case of aluminum or antimony added in a similar manner, the effect of pouring temperature was subordinate to that of the added element.

Conclusion

In conclusion, then, it is evident that careful temperature measurement is an essential factor in the successful operation of a foundry. Two dissimilar types of thermocouples now being used in a number of foundries have been discussed, and another type which has proved satisfactory in this investigation has been described. It has been shown that, for the different types of the test bars cast, optimum physical properties of the red brass alloy 85-5-5-5 were obtained at a pouring temperature of 1150 °C (2100 °F), but it is recognized that in commercial practice other factors, some of which are listed, must be considered in the selection of the proper pouring temperature or range. High-grade metal, after being melted under the proper conditions for the type of furnace used, may still produce faulty castings and unduly increase the supply of scrap on hand. This is due, in part at least, to an improper selection of the maximum heating temperature and the pouring temperature or to prolonged "soaking" of the molten metal at high temperature. The proper selection of the various temperatures to which the metal is subjected during melting and casting and the accurate measurement of these temperatures are essential factors in the production of good castings.

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A Simple Method of Thermal Analysis Permitting Quantitative Measurements of Specific and Latent Heats*

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The method of thermal analysis, so important in the development of metallographic science, has of recent years been falling into disuse because of the introduction of other physical methods giving results which are easier to interpret, and which can be used for the study of either equilibrium or transitional conditions since they do not require a continuously changing temperature. Nevertheless, thermal analysis remains useful in the study of reactions that take place rapidly, and the simplicity of the experimental technic and the general availability of the apparatus involved are points in its favor.

Theoretically, thermal analysis is capable of giving specific and latent heat measurements, and therefore should permit the study of reactions on a more fundamental basis than any other method. It is, however, difficult or impossible to obtain quantitative heat measurements from cooling curves obtained in the usual way. Even if the furnace containing the sample is cooled or heated at a linear rate, or if a gradient furnace is employed to maintain a constant rate over a large range of temperature, the heat flow from or to the specimen depends on its previous history, for the difference of temperature between the specimen and its surroundings varies. The emissivity of the surface of the specimen, moreover, is unlikely to be constant. The able mathematical analysis by Russell,[1] although it prevents misinterpretation of data, has an effect rather the reverse of that intended, and leaves the reader doubtful of the possibility of ever obtaining quantitative results from thermal curves.

Nothing can be done to apply thermal analysis to the study of equilibrium conditions of reactions that are not completed at rates of temperature change above about 1 °C per minute, and this unfortunately excludes most solid transformations in alloys.† For the determination of liquidus temperatures and peritectic or eutectic horizontals, the ordinary cooling curve is often sufficient, because all that is necessary is the temperature of inflection, and quantitative heat measurements are meaningless because of segregation and the lack of approach to equilibrium. In the rather limited field where reactions are fast enough and where quantitative heat measurements are desired, the following method will be found useful. It is suitable for the determination of heats of reactions that occur with reasonable rapidity, and rates of transformation, precipitation, or ordering on progressive heating or cooling. The method also seems to have utility in the determination of specific heats with fair accuracy and great ease, employing only apparatus available in every metallurgical or physical laboratory.

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† Thermal analysis can be sometimes used to determine the presence or absence of a phase after long annealing to obtain equilibrium, for if the sample is then cooled or heated at a convenient rate an arrest will appear if the phase is present at some temperature characteristic of the rate of cooling, even though it is far removed from the equilibrium temperature.

Principle of Method

Briefly, the new method consists in placing the specimen with its thermocouple in a refractory container of low thermal conductivity and placing this in a furnace the temperature of which is maintained a constant amount above or below the specimen temperature. This is easily managed by opposing the electromotive force of the specimen couple to that of a couple at the outside of the container, and feeding the resultant electromotive force to an automatic temperature controller of ordinary design. Alternatively, a differential couple may be used, independent of the specimen couple, with one junction inside and another outside the container.* In this way a constant temperature gradient is maintained across the container walls. Since the thermal conductivity of the refractory remains constant at a given temperature, the heat flow through it will be constant, and so the heat received or lost by the specimen in a given elapsed time will be constant. Obviously, therefore, the time taken for the specimen to move through a given temperature interval will be proportional to the heat absorbed or evolved.

Actually, the conductivity of any refractory does not remain exactly constant as the temperature changes. Neither does the emf difference of opposed thermocouples remain independent of temperature; consequently the heat flow varies slightly with temperature. However, a given container can be calibrated over a range of temperatures by use of a mass of known specific heat and will give reproducible quantitative results.

Fig. 1 shows a setup which has proved satisfactory. The specimen (0.75 in diameter, 1.5 in long) fits closely in a container with walls 0.375 in thick, turned on a lathe from a piece of Armstrong "Non Pareil" insulating brick. This material is said to have a thermal conductivity of 0.00028 cgs unit at 150 °C and 0.00044 at 870 °C, the maximum temperature at which it should be used. When a temperature difference of 60° was maintained, the heat flow through this container varied between 0.92 cal per second at 200 °C and 1.23 at 600°. For higher temperatures a crucible of Armstrong LW20 insulating brick (conductivity = 0.0006 to 0.0008 cgs unit at 540° to 1315 °C) was used. Both these materials were found satisfactory, but obviously any insulating material of suitable refractoriness, mechanical characteristics and constancy could be used. The container was given a wash of Alundum cement to fill surface pores. It was found necessary to dry it by heating immediately before use, as it was distinctly hygroscopic. The furnace consisted of an Alundum core, 2¼ in in diameter, uniformly wound with Nichrome wire. To obtain a cooling rate sufficiently rapid for thermal analysis very little lagging (½ in) is necessary, but a furnace for heating curves alone may be well insulated. The container is supported on Nichrome spacers to allow free circulation of air around and below it. Edmunds[5] has described an important modification of this apparatus. (See pages 981-983 of the present volume.)

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* The differential couple is to be preferred for accurate determinations of specific heat. The two-couple method is perhaps simpler to construct and use but it necessitates a controller of high resistance (at least 300 ohms). The ordinary potentiometer controller is of low resistance and will affect the main thermocouple readings appreciably when it is slightly out of balance during the control cycle. It is, of course, important that the controller have a short cycle and that the furnace have as little lag as possible. Control of the average temperature within 0.5 °C is desirable, but a reproducible cycle larger than this is harmless if of short duration. If the controller is compensated for cold-junction temperature changes (as are most commercial instruments) it is necessary to eliminate this or to place a thermocouple with one junction in ice and the other at instrument temperature, connected in series with the emf to be controlled.

Specific Heat Measurements

If it is desired to make quantitative heat measurements, it is necessary first to calibrate the container by determining its rate of heating when empty and then with a simple of known specific heat. Copper is a suitable standard, since it undergoes no transformation and its specific heat is known fairly accurately over a wide range of temperature.[2]

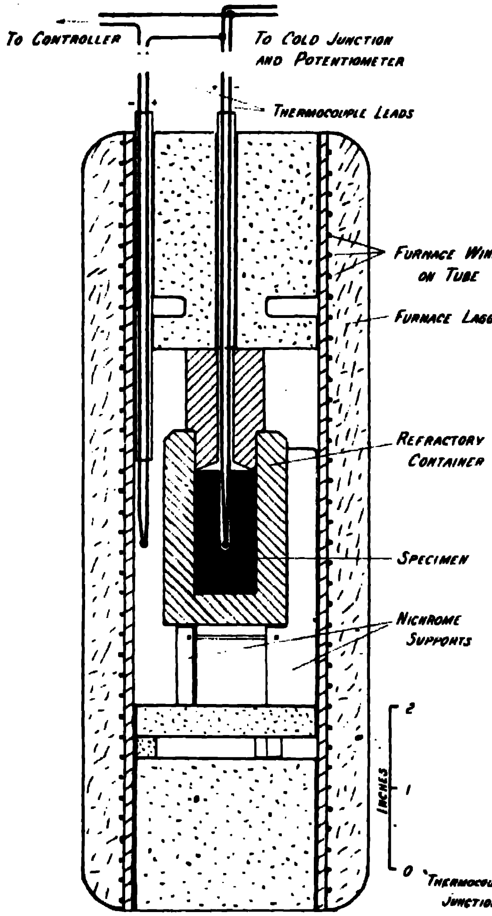

Fig. 1.

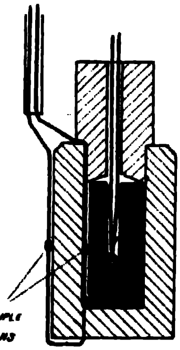

Fig. 2.

Fig. 1. Apparatus for thermal analysis.

Fig. 2. Arrangement of differential couple for controlling temperature gradient across container.

The rate of heat flow through the container is equal to the product of its conductivity and a constant depending on its size and shape, multiplied by the temperature difference between its inner and outer surfaces. With a given container the first two factors are constant and the temperature difference is maintained constant experimentally. The resulting constant heat flow serves to supply the specific heat of the sample, its heat of transformation. if any, and the specific heat of an indeterminate part of the container itself, *i.e.*,

$$H \times \Delta t_1 = \Delta T_1 \times C_1W_1 + L_1W_1 + \Delta T_1 \times C_rW_r \tag{1}$$

where H is the heat flow per unit time; C_r, C_1 and W_r, W_1 are the specific heats and masses of the effective part of the container and of the specimen, respectively; ΔT is the change of temperature in time Δt; and L_1 is the latent heat of any transformation that may occur in the temperature range of ΔT.

If a second sample of heat capacity C_2W_2 is substituted, then (if no transformation occurs in either sample so that latent heat may be omitted), by the use of the equation for the empty container ($H \times \Delta t_r = \Delta T_r \times C_rW_r$)

$$\frac{C_2W_2}{C_1W_1} = \frac{\dfrac{\Delta t_2}{\Delta T_2} - \dfrac{\Delta t_r}{\Delta T_r}}{\dfrac{\Delta t_1}{\Delta T_1} - \dfrac{\Delta t_r}{\Delta T_r}} \tag{2}$$

The figure $\dfrac{\Delta t}{\Delta T}$ is the slope of a time-temperature curve, or the figure obtained directly for an inverse rate curve* in the usual way. In the equations above, the subscripts r, 1 and 2 denote respectively this figure for the empty container and for the container with specimens 1 and 2. The heat capacities of samples are thus directly proportional to the values of $\dfrac{\Delta t}{\Delta T}$ after they have been corrected by subtracting a blank reading obtained from a heating or cooling curve of the container alone. Because of the shape of the container and the non-uniform temperature gradient in it, the correction will be greater on cooling than on heating. When latent heats are involved it is necessary to determine H at the appropriate temperature. by substituting the experimental times from a blank and standard run; *i.e.*,

$$H = \frac{C_1W_1}{\dfrac{\Delta t_1}{\Delta T_1} - \dfrac{\Delta t_r}{\Delta T_r}}$$

The latent heat of a transformation causing an arrest at constant temperature is directly proportional to the duration of it ($LW = H\Delta t$ when $\Delta T = 0$). If a transformation occurs over a range of temperature, its latent heat will appear as apparent specific heat.

It is obvious that a highly polished surface on the sample would result in an appreciable temperature difference between it and the inner walls of the container. For this reason it is desirable to roughen the surface of the specimen and to coat it with a material of high emissivity unless it is to be in actual thermal contact with the container.* If the junction of the inner controlling couple is against the wall of the container, the sample will lag, but nevertheless will receive the standard heat flow, except after an arrest. For this reason the differential couple is to be preferred in specific heat measurements. Another disturbing factor lies in the fact that the temperature gradient within the container is not linear, since the temperature is changing, and the container correction therefore varies with heating rate. These and other effects, however, are small and are largely eliminated if the standard sample has a size, heat capacity and emissivity of the same order of magnitude as the other samples to be tested.

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* Most conveniently this is the time for a temperature change equivalent to an emf change of 0.05 mv with a Chromel-Alumel thermocouple rather than a specific temperature interval. In making the time measurements for an inverse rate curve, whether these are to be used for specific heat measurements or ordinary thermal analysis, it is desirable to have the galvanometer zero mark directly on the face of the clock. The clock (preferably reading in hundredths of a minute instead of seconds) is placed alongside the potentiometer at a convenient angle for reading, and the light beam reflected down to it by a mirror. This makes it unnecessary to change the focus of the eye when passing from the galvanometer index to the clock, and readings good to ± 0.01 min are readily obtained over prolonged periods with little eye fatigue. Entirely automatic devices for plotting inverse rate curves have been constructed. A good commercial recording potentiometer will give a time-temperature curve, the slope of which can be measured with sufficient accuracy for many purposes.

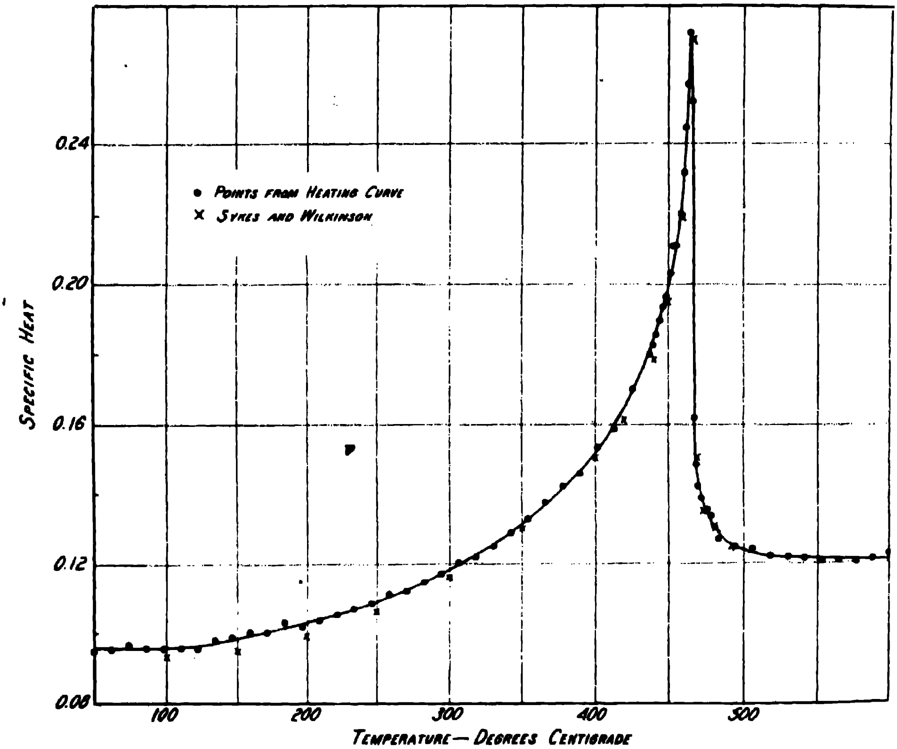

Fig. 3. Specific heat of beta brass as obtained from a heating curve.

Fig. 3 shows the specific heat of beta brass obtained from a heating curve. The sample weighed 86.6 grams and contained 48.10 per cent zinc by weight. With the container described above and a temperature difference of 60 °C (controlled with a differential couple) the assembly heated at a rate of about 4 °C per minute at the beginning, decreasing to 2.5 °C per minute where the heat absorption was greatest. Although t and Δt were recorded every 0.05 mv, the points plotted are based on the time to pass the entire distance between them. This represents 0.5 mv

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* A saturated solution of copper nitrate, dried on the surface of the specimen and heated to 300 °C provides a good black on copper alloys except in reducing atmospheres. Commercial heat-radiating paints are available and probably would be satisfactory.

(about 12 °C), except in the range 440 to 480 °C, where $\Delta T = 0.1$ or 0.05 mv. The percentage accuracy naturally decreases with smaller intervals. For comparison, a few points are shown in Fig. 3 read from the curve for a sample with 49.70 per cent zinc given by Sykes and Wilkinson.[3] The agreement is remarkably good in view of the simplicity of the present apparatus and the complicated nature of the electrical method used by these investigators. With the electrical method it is difficult to obtain points less than 10 °C apart: the new method will give readings over a much smaller temperature interval—down to a fraction of a degree if sufficiently sensitive temperature and time-reading devices are employed. Moreover, it can be used for measurements on cooling as well as on heating.

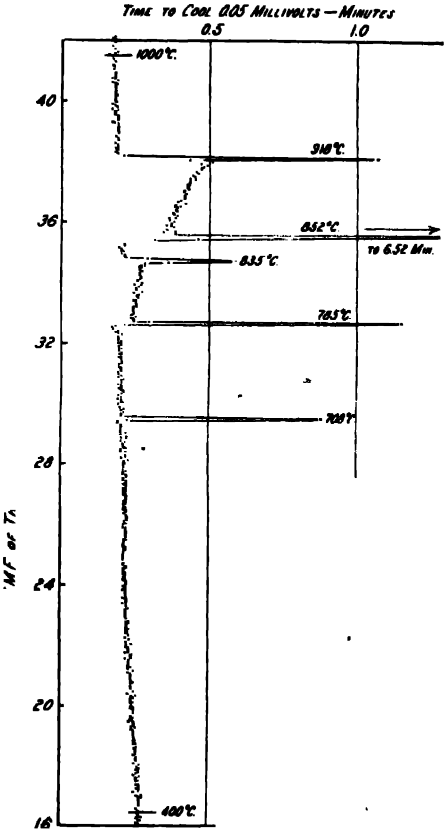

FIG. 4.

Cooling curve of copper-silicon alloy containing 6.3 per cent silicon. Note absence of accelerated cooling following arrests and constancy of cooling rate at all temperatures.

Cooling Curves

Even if quantitative heat measurements are not needed, as in the ordinary thermal analysis of alloys to obtain transformation temperatures, the method of control is useful in that the heat flow from the specimen is maintained constant and there is not a rapid removal of heat after an arrest. The furnace temperature is held constant throughout an arrest and does not commence to fall until the specimen itself cools. As a result, temperature gradients within the specimen and along the thermocouple are smaller and arrests are sharper. Interpretation of the curves is very easy, for they directly reflect the changes taking place in the specimen. The decrease in cooling rate at lower temperatures that is characteristic of ordinary curves is completely avoided. If no arrests occur, the rate of cooling over the whole temperature range varies only to the extent that the thermal conductivity of the refractory and the specific heat of the sample change. The rate of cooling or heating can be changed at any time by merely changing the setting of the temperature-difference controller. The new method obviates the necessity for gradient furnaces or linear control devices and is much simpler than any of them.

Fig. 4 is an example of the type of cooling curve obtainable. This is of a 150-gram sample of a copper-silicon alloy containing about 6.3 per cent silicon. It was placed in a container like that of Fig. 1, but 1¼ in in internal diameter and made of LW20 refractory. The various arrests are caused respectively by the liquidus, peritectic formation of beta, kappa formation, beta decomposition and gamma formation. Note the sharpness of the arrests and the virtual absence of accelerated cooling at their termination. The decrease in latent heat resulting from the decreased amount of alpha solidifying in a given temperature range, as the horizontal spread between solidus and liquidus increases, is clearly shown. The specific heats of the alloy in the liquid, alpha + beta, alpha + gamma, and alpha + delta fields are approximately the same, while in the kappa + beta region the progressive rapid formation of kappa from beta contributes latent heat and so increases the apparent specific heat of the sample in this range.

Summary

The specimen is placed in an insulating refractory container across which a constant temperature gradient is automatically maintained. Heat flow to the sample depends only on the constants of the container, which may be determined by the use of a sample of known specific heat. The time taken to cool or heat through a given temperature interval (after a blank correction) is directly proportional to the heat capacity of the sample, and the duration of an arrest is directly proportional to the latent heat. The method of control eliminates accelerated cooling following prolonged arrests and provides a simple way of obtaining a constant cooling rate at all temperatures, thus replacing elaborate gradient furnaces. Examples are given, including a determination of the specific heat of beta brass.

Discussion

Gerald Edmunds, Investigator, Research Division, The New Jersey Zinc Company: Dr. C. S. Smith kindly lent us a copy of his manuscript describing this method of thermal analysis. We have since constructed an equipment based upon the principles described by him, but with a few alterations which will be described.

Our equipment contains, instead of the refractory container (shown in Dr. Smith's Fig. 1), two concentric Nichrome cylinders, Fig. 5, inside of which is placed a very thin wall crucible, either of graphite or other suitable material. To the Nichrome cylinders are welded several Alumel wires, thus providing multijunction thermocouples which operate a controller for the furnace windings and thus maintain the temperature difference between the Nichrome cylinders. An additional thermocouple is used for measurement of the melt temperature.

An internally wound Nichrome furnace with a small amount of heat insulating material is used. This type of furnace is desirable on account of the proximity of the winding to the thermal shield and the low thermal inertia of the furnace, thereby providing flexible furnace control. This furnace winding was formed on a 2½″ diameter collapsible mandrel and covered with $\frac{5}{16}$″ of Alundum cement. After drying and smoothing this was fitted into a 3″ diameter Alundum tube which serves

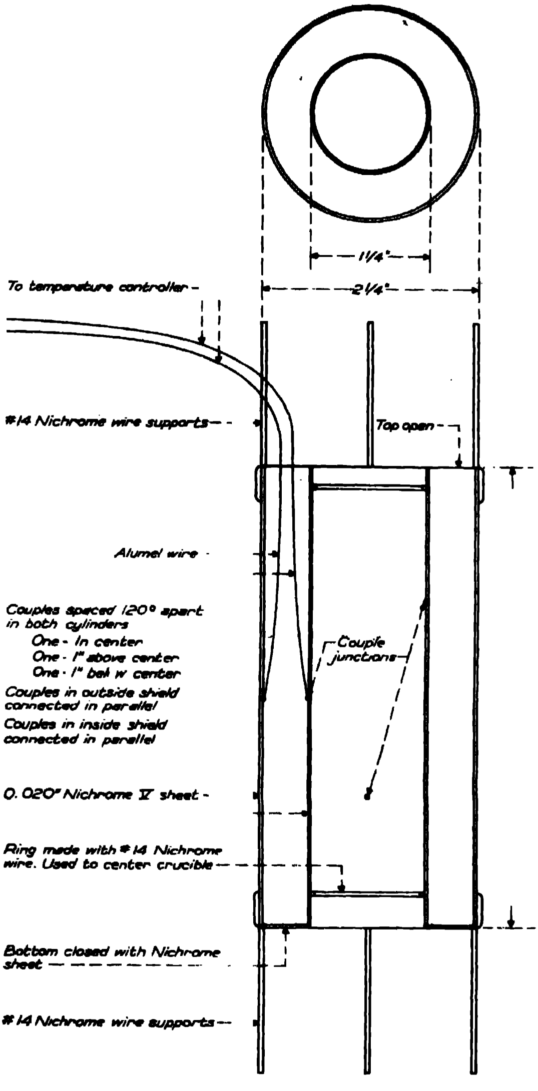
1 1/4"
2 1/4"
To temperature controller
#14 Nichrome wire supports
Top open
Alumel wire
Couples spaced 120° apart in both cylinders
One - In center
One - 1" above center
One - 1" below center
Couples in outside shield connected in parallel
Couples in inside shield connected in parallel
Couple junctions
0. 020" Nichrome V sheet
Ring made with #14 Nichrome wire. Used to center crucible
Bottom closed with Nichrome sheet
#14 Nichrome wire supports

FIG. 5. Nichrome cylinders assembly.

as a support for the winding. The tube was placed in an 11" diameter sheet iron shell with Transite ends. No heat insulating material was used.

One of the major advantages of Dr. Smith's method is that it makes possible the detection of any small heat effect at a temperature only a few degrees below that at which a major effect has occurred. With the conventional differential thermal analysis method sufficient stabilization after a large heat effect for the detection of a small one may not occur until the specimen has reached a temperature as much as 30 to 50 °C from that at which the large effect occurred. Dr. Smith's Fig. 4 shows only slight irregularities following major heat effects.

While our construction has not been compared directly with that used by Dr. Smith, calculations indicate that the heat capacity of the thin Nichrome cylinders is less than equivalent refractory insulation. This leads to a closer control of the temperature difference and reduces further the time required for stabilization of conditions following a major heat effect from the specimen.

This effect of heat capacity was noted on cooling and heating curves on pure zinc during our first use of the apparatus, at which time the Nichrome cylinders rested upon a refractory block. Substitution of Nichrome legs, as used by Dr. Smith on his apparatus, resulted in a marked decrease in the time required for stabilization.

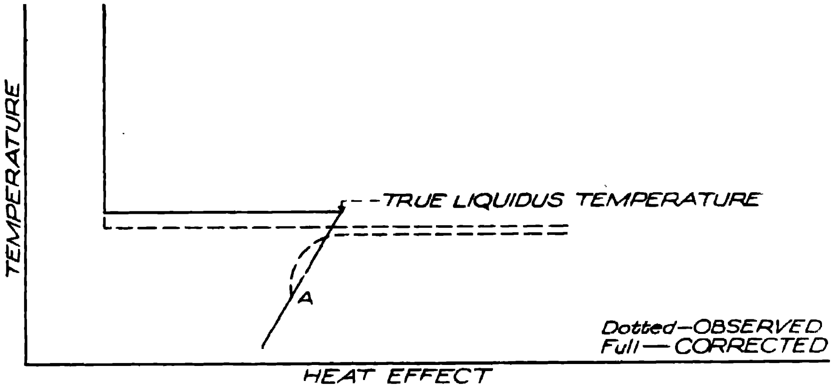

FIG. 6.

The cooling curves obtained by any method, whether using the new method of control or not, generally show a very large thermal effect at the beginning of freezing. This is apparently due to undercooling of the melt resulting in the evolution of much heat when crystallization begins. In a curve such as Fig. 4 in Dr. Smith's paper the time of cooling 0.05 mv. at 918 °C. amounted to about 1.1 minutes whereas cooling with crystallization at the normal rate required but 0.5 minute just afterwards. Had crystallization started immediately upon reaching the liquidus the heat effect would have been so distributed as to continue the curve (A), Fig. 6, upward about two of the 0.05 mv. divisions and the curve in this neighborhood would then be as shown in Fig. 6. This type of correction has been made to all of our curves and has often been found to be of major importance, since supercooling of many degrees frequently occurs.

Reply

Mr. Edmund's comments are a valuable addition to the paper. His design of apparatus constitutes a decided improvement over the original one for certain purposes. The internally wound furnace would respond much more quickly than the conventional design and permit close control of temperature difference when using straight on-off control, hence is particularly desirable when readings are to be made continuously over a wide temperature range. The double Nichrome cylinder assembly is to be preferred for general metallurgical thermal analysis on account of its ruggedness, but I believe that solid refractory insulation should be used for measurements of specific heat, since it is more constant in its characteristics and changes less with temperature.

The correction of liquidus temperatures suggested by Mr. Edmunds to allow for undercooling is fundamentally sound. It should be applied to cooling curves determined by any method but is precise only when the rate of heat flow is constant, as with the present apparatus. It is easier to make this correction graphically on a straight time-temperature curve than on an inverse rate curve. The true liquidus temperature on a time-temperature curve is just the point of intersection of the curve for the liquid state with the extrapolation of the part of the curve that corresponds to the liquid plus solid state after the first arrest due to supercooling.

Many years ago White[6] used two thermocouples in a furnace for thermal analysis and attempted quantitative interpretation on the basis of temperature differences. The present scheme is novel only in the use of insulation and automatic control of the temperature difference. This results in constant and reproducible heat flow instead of the variable conditions that exist when a naked crucible is placed in an indefinitely cooling furnace.

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Relation of Uniform Pyrometer Records to Uniform Products

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The relation of evidence and proof, of shadow and substance, is, in effect, substantially the relation of pyrometer and product in industrial heating practice. There is a difference, not generally sensed in shop practice in the several industries, between simple control of temperature and control of other equally important factors that affect uniformity of the product itself. Uniform temperature is essential for uniform products; but heating a chamber uniformly and uniformly heating or cooling an individual piece, or a charge of many pieces, within that chamber are distinct problems. The real test of the operation in the shop is in the uniformity of the ultimate product, just as it is in the kitchen of the household.

Pyrometric practice in the metallurgical, ceramic and chemical industries is generally not up to the high standard of operation conceived by instrument manufacturers. Emphasis on temperature control frequently leads to disregard of the influence of other factors affecting uniformity of the product which are just as important as factors related to means for indication and control of temperature. Uniformity is a relative term. Absolute uniformity is rarely, if ever, attained. Uniformity of products according to commercial standards can be maintained only by proper coördination of all factors affecting uniformity, of which temperature is but one.

Heating in one way or another affects the quality and cost of practically all manufactured products. Its influence is far-reaching, particularly in metal and ceramic products. Yet it is doubtful if there is another industrial process of equal importance so poorly practiced, so misunderstood, so influenced by the inertia of tradition, or so susceptible to irrelevant changes.

Continual variation in color of ceramic products, or in the grain size, physical properties, or surface condition of metallurgical products—made with equipment provided with automatic temperature control—indicates the need and possibility for better heating practice.

The relation of pyrometer and product frequently is either not recognized or is misunderstood, in the relatively academic atmosphere of the laboratory or the classroom. There, it is reasonable to assume, all factors affecting uniformity should be considered as a basis for developing the proposition that the real test of uniformity is in the product, in the manufacture of which pyrometry is but a means to an end. Reference to this important subject is conspicuous by its absence in most of the textbooks of acknowledged authorities.

A significant illustration of the prevalent viewpoint on the relation of pyrometry to quality of product is afforded by a certain specification for heat-treating equipment recently issued by an outstanding source thoroughly circumscribed by technical control.

The specification disposed of the fundamental requirements for operation of the equipment—in terms of heat-treated product—in less than two lines. Yet, there were about four pages devoted to minute, detailed specifications of the mechanical characteristics of the temperature-control equipment. Other essential factors, in addition to temperature, which affect uniformity of the product were ignored in an effort to indicate preference for specific means of indicating the temperature of the end of a couple which might or might not represent the actual temperature of the product itself.

There is ample opportunity for improvement in the time-honored practice in the mass-heating methods of steel-casting and malleable-iron foundries; sheet steel, wire, and other steel rolling mills; brass and copper rolling mills; copper refineries, and many others. The long-established practice of individually heating and cooling structural steel shapes and railway rails is in marked contrast to mass methods of heating and cooling bars, shafts and other expensive alloy-steel products. If it is right in one case, it is wrong in the other.

Equal opportunity is afforded in the ceramic industries wherever inequalities are made apparent by differences in color of the finished product, whether in the stock pile of the producer, in the storage yard of the dealer, or in the ultimate structure. Usually, however, there is reasonable control of production in mixing, forming, drying, and handling—up to the time of loading the product in the kiln for burning.

The practice in the red-brick industry of drying the bricks individually while separated on a pallet, and then attempting to burn them uniformly while closely piled in a scove-kiln, comprising one or two million bricks, results in the well-known lack of uniformity of size, shape and color of the finished product.

One economic test of the value of new materials, or base products, is the uniformity of the products made from them. Specification for control of the structure of the material by heating and cooling is about all that can be expected from, and usually about all that is supplied by, the producer. Yet products made from the same material, and of the same weight, may require different methods of control because of a difference in the time and rate of heating and cooling incident to variation in shape, section or dimension of the individual piece, or because of a difference in method of loading. A ball, a cube, or an irregular product such as a milling cutter, gear or propeller, may require different methods of transferring heat to or from the individual piece, and therefore different methods of control.

It is apparent that much of the inequality frequently attributed to the material of which the products are made is actually due to unsound shop practice of the fabricator in heating and cooling. It is not necessarily a matter of equipment, fuel, electricity, or temperature control. Basically, it reflects a traditional custom in the shops to disregard the influence of physical factors that affect uniformity. To the uninitiated it seems strange that such conditions should exist in the light of our outstanding modern technical development.

Better results will follow when we have men in the shops who are better educated to practice one of the oldest industrial arts, one that has more influence on quality and uniformity than any other fabricating process. It has its roots in the ceramic practice of the ancients log before the machine age, or even the metallurgical age. There is need for trained production specialists and supervisors of the important heating and cooling operations. The present industrial situation is as though the Army had many dieticians to prescribe suitable diet, but not enough skilled cooks to prepare the the food.

The problem of uniformity is particularly pressing today because of its relation to the program for national defense. Uniform ordnance equipment, and in fact uniformity in all material and equipment, is essential from a military point of view. As quality and useful service are materially influenced by many industrial heating operations, it is apparent that the highest possible practical standards of uniformity in production should be maintained as a matter of course.

Yet, strange as it may seem, the Army and Navy never have been armed with ordnance, ammunition and auxiliary equipment of desirable uniformity. They were not produced in this country during the World War, either for ourselves or for our allies. They cannot be so produced today on a large scale with prevalent methods of production. They will not be produced until industry is educated to appreciation of the fact that much of our shop practice is out of step with development of science in the laboratory, and that uniform pyrometer charts should not be acceptable as *prima facie* evidence of uniform products.

Industrial heating is a bottle-neck in production and is also the weakest link in quality and uniformity in the industrial preparedness program. For this reason, it affords an unusual opportunity for development of higher standards of uniformity, which should have a pronounced effect on the pyrometric practice of the future.

Buyers of large quantities of metal and ceramic products are continually confronted with variation in quality and uniformity of equipment and products, manufactured in different shops from identical specifications. That each shop usually offers evidence of uniformity in temperature charts clearly indicates possibility of irregularity in the product not disclosed by the pyrometer.

Industry is becoming increasingly aware of this through customer demand for higher standards of quality, and particularly uniformity. It is developing the idea that production specifications should be amended in some manner to afford better control of the ultimate product.

"Process Specification" has been suggested as a means to the desired end. Misunderstanding of intent, and the mental inertia that resists change, probably account for restricted acceptance, even in the light of the possibilities conclusively demonstrated in practice with a great variety of products in different industries.

The proposed "Process Specification" is in no way intended to affect the metallurgical, ceramic or chemical specification, nor to indicate how the producer or fabricator is to do his job. It permits either of them to write his own ticket for any desired standard of quality, whether it be good or poor, with any composition of material or method of processing that he may prefer. It is proposed, as an amendment to the laboratory specification, to effect better control of the individual heating and cooling operations, whatever they may be, to a degree of uniform shop practice that will reasonably insure uniform products from day to day in the individual plant, or from different plants producing under the same specifications.

It is primarily intended to indicate preferred methods of exposure (or loading) in heating and cooling; reference to preferred rate of heating and cooling; time of exposure, which determines the actual temperature of the product; atmosphere, and any other essential factors that may guide the production staff in an effort to produce each piece as nearly like every other as may be practical to meet specific requirements. In short, it is intended to encourage a new conception of uniformity, *i.e.*, "Uniform products—either uniformly good or uniformly poor—but always uniform."

Need for some such reform is apparent in the light of overwhelming proof of variations in base material or fabricated products, regardless of the evidence of pyrometer charts that such variations do not exist. In proportion as the proposal, or its equivalent, is accepted better pyrometric practice, and intelligent use of more and better pyrometers will be developed.

Industry in general, and the instrument industry in particular, would be better off if more thought were given to the condition of the biscuits in the oven, in addition to means for indicating temperature on the oven door. Most good cooks realize that food products vary in different sections of the modern gas and electric oven, even though the thermometer may indicate uniformity. Yet by and large, food products, whether produced on a small or large scale, are usually more uniform than most manufactured products subject to heat in the process of production.

Production men have much to learn from the chef in the operation of industrial heating equipment, which involves many variable factors, including the use of pyrometers.

Much of our shop practice seems to be not so far removed from that of the ancients. They occasionally depended on the moon, or sacrificial prayer for guidance. We frequently streamline the performance with a star-gazing process of watching the pyrometer and hoping for the best. "By their works ye shall know them": we are ultimately judged by what we have done to the product, rather than by what we say of temperature control.

The industrial heating and instrument industries should welcome and encourage such development. It will stimulate a better understanding of proper methods of heating and cooling industrial products, and automatically open new fields for development of better instruments.

Possibility for improvement is illustrated by outstanding accomplishments of the automotive industries in establishing the higher standards of uniformity which are necessary for the proper performance of their products. These industries have forced improvements in many other industries that otherwise would have been likely to resist change. Such improvements have been effected in ball and roller bearings, condenser tubes, steel sheets, wire, and a great many other products, in addition to an astounding development of new production equipment. All of this has a social and economic value in the form of better and cheaper products, increased employment, and higher standards of living.

The coöperation of many groups will be required to develop a better understanding of the *de facto* relation of uniform temperature charts to uniform products.

Pyrometric Cones

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Pyrometric cones are used by the ceramic industry for determining the maturity of the ware. They are slender trihedral pyramids made of a mixture of minerals similar to those of which ceramic bodies are compounded so that they react thermochemically in much the same fashion. This similarity of composition makes the cone a guide in the firing of ceramic products.

Historical

Pyrometric cones were first commercially produced in Germany by Seger in 1886; Lauth and Vogt made cones for their own use at Sevres as early as 1882, but they did not make a complete series nor did they offer the cones for sale. Seger's original series was subsequently materially extended by Seger himself. Cramer and Hecht later covered higher and lower melting temperatures. There is now a complete series of cones from 022 through 42, making 61 in all. Some German cones were used in the United States in the early nineties, although Langenbeck made cones for his own use as early as 1887 at the Encaustic Tiling Company, Zanesville, Ohio. Orton began making cones commercially in 1896 in the ceramic department at Ohio State University. Cones are now made in England, Germany, France and America.

General Description

The cones are so compounded from mixtures of china clay, feldspar, whiting and flint that they deform under the influence of heat at regularly advancing temperature intervals. In the compositions where these minerals will not serve alone, such fluxes as the sesquioxide of iron and certain prepared glasses are added.

When compounding a given cone body the components are carefully weighed and mixed dry in a ball mill. A representative sample of the batch is made into cones and tested against standard cones. The deformations of the test cone and the standard cone must be identical; if not, a correction is made in the batch. In case the deformations are not identical after the correction has been made and tested, the batch is further corrected until the action of the cone under test and that of the standard cone are identical. The deformations of the cones must check in both a gas-fired kiln and an electric furnace. The series is formulated to produce a scale of melting points with approximately 20 °C-intervals.

The American Society for Testing Materials was not satisfied with the terms "fusion point" and "deformation temperature," so has substituted P. C. E. (pyrometric cone equivalent) to designate cone end-points. A clay is said to have a P. C. E of cone 30 when it deforms under the same heat treatment as does cone 30 under the conditions prescribed by the American Society for Testing Materials. This Society was the first to insist on the dimensional accuracy of cones. The desired accuracy has been produced by a plastic press process.

Cones are made in two sizes. The small cones are 1⅛ inches in length and 9/32 inch on the base. The large cones are 2⅝ inches long and ⅝ inch on the base. Both the large and the small cones are made over the entire series.

Effect of Furnace Atmosphere

Cones not only indicate the maturity of the ware but also to a degree indicate the character of the kiln atmosphere. Ceramic wares should normally be fired in a clean atmosphere and one having considerable excess air, that is, with an atmosphere containing from 25 to 50 per cent excess air at high fire up to one with more than 100 per cent excess air during the early stages of the fire. The atmosphere should be reasonably free from sulfurous gases. There are conditions where, to get certain desired effects in the ware, a reducing atmosphere is desired. These conditions are, however, exceptional.

Sulfurous atmospheres and reducing atmospheres adversely affect the accuracy of pyrometric cone deformation. As explained previously, each of the cones is compounded of silicates, oxides and glasses in varying proportions. The effect of the atmosphere on the different cones is specific. The low-temperature cones, with their low-melting lead glass, are quite susceptible to reducing atmospheres, and this also applies to the intermediate series containing iron oxide. The iron oxide exists in two forms depending upon the atmosphere to which the cone is subjected; thus cones containing this oxide deform quite differently, depending upon the valence of the iron. Iron also acts as a catalyst in a reducing atmosphere and can deposit graphitic carbon in the body of the cone. Sulfur gases are strongly absorbed by the iron-bearing cones. These conditions will cause the cone to bloat due to the forming of a refractory shell, while the interior of the cone will fuse and drain.

Some of the more refractory cones perform in a characteristic way when the temperature rise is intermittently advanced toward the end of the fire. Under these circumstances a condition known as freezing occurs. Smith[1] has found that freezing may be due to a separating out of silica in the form of cristobalite. It amounts to a devitrification of the glass phase which causes the cone to stand after it should normally have gone down.

While these conditions are not conductive to cone sensitivity, they may teach the informed operator that his kiln atmosphere is wrong or that his heat is not advancing regularly.

The Cone Series

For convenience, cones are divided into four series. These series are roughly divided along lines of composition. The soft series was developed, after the Seger series, by Hecht. A lead borosilicate glass is the characteristic component of this series. The soft series, called by the Germans the zero series, covers the heat treatment of overglaze colors, gold, and lusters on china and glass. This series has been considerably modified in that the lead frit is now used alone only in the lower numbers. As Cones 017, 018 and 019 are used in the decorating kilns by the potters, the lead frit would be too sensitive to reducing gases. These cones should be used only in muffled gas kilns or in electric kilns.

The cones of the low-temperature series have the Cramer frit in the batch. The Cramer frit is a soda-lime-borosilicate glass. The low-temperature series contains no lead oxide in the batch, but does contain iron oxide and is often called the red series. In the presence of reducing and sulfurous gases these cones act erratically as stated before. They will develop a hard shell with a molten interior which causes bloating. An iron-free series is now being developed which shows none of these characteristics. Shale products, the low-fired glazes and some art pottery are fired in this range of low-temperature cones.

The intermediate temperature series was the original Seger series. It has been modified to form a more uniform temperature gradient. It is compounded of clay, flint, feldspar and whiting. These cones cover the requirements of a variety of clay wares, such as buff-firing clays and artificial pottery bodies, hard ceramic glazes, salt glazes and Bristol glazes.

The high-temperature series is used for testing refractory clays and products. The original series contained cones 21, 22, 23, 24, 25. All five of these cones went down under nearly the same conditions; variations in firing had more influence than the differences in composition. The middle number, 23, is now made and it divides the space between cones 20 and 26 satisfactorily.

Cone Deformation

A cone deforms when sufficient liquid phase has been formed to render the body physically unstable. Because of the viscous character of the liquid the cones bend very gradually. The viscosity is due largely to the high silica content of the melt. The amount of the melt and its viscosity will vary widely with different cone compositions.

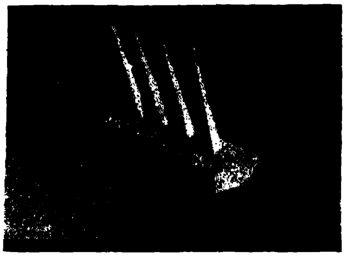


FIG. 1. Plaque of large cones (as set in potter's kiln).

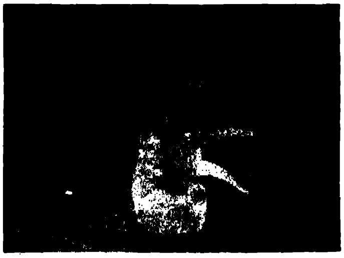


FIG. 2. Cones deformed (as taken from potter's kiln).

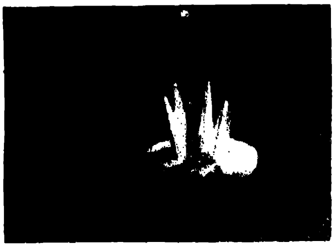


FIG. 3. Small cones set in plaque for standardization in carbon resistance furnace.

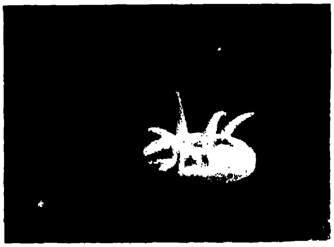
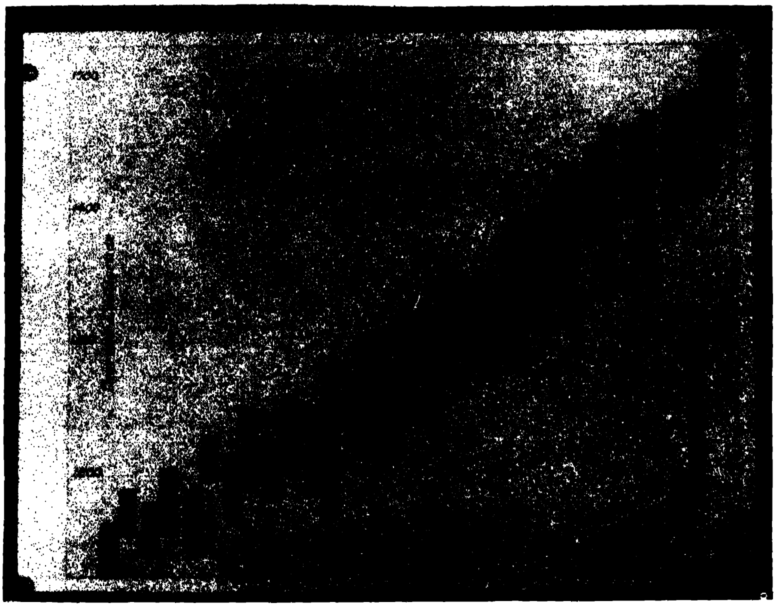


FIG. 4. Cones in process of standardization. (Cones on either side of erect cone are the cones under test. The others are standard cones.

The softening of pyrometric cone bodies is the story of eutectics and solution in the eutectic. Both Sosman[2] and McCaughey[3] have explained the thermochemistry of cone deformation. McCaughey describes the melting of a silicate mixture essentially as follows:

In mixtures of minerals, the melting phenomenon generally starts at a lower temperature than the melting point of any single mineral, the initial melt that forms having the eutectic composition. The amount of melt forming at the eutectic temperature depends upon the composition of the mineral mixture. A mixture of minerals of the composition of the eutectic would melt completely at the temperature of the eutectic if the conditions were favorable; but because of unfavorable grain size and mixture, and of the high viscosity of silicate glasses with consequent slow diffusion, the eutectic composition melts or sweats out slowly. As the composition of the mineral mixture departs from the composition of the eutectic, less and less liquid phase makes its appearance at the eutectic temperature.



Bending intervals (when heated slowly, black, and rapidly, gray).

After a liquid of the eutectic composition has made its appearance, the second stage of cone deformation proceeds, namely, dissolving of the solid components by the eutectic liquid. This phenomenon covers a temperature range varying with the amount of the undissolved minerals present. The larger the amount of undissolved mineral remaining after the eutectic has melted, the greater the temperature range in the second stage of melting. As more and more of the undissolved minerals pass into solution in this second stage of melting, the amount of melt increases, and finally enough is formed for the body to soften gradually, according to the viscosity of the melt. Applying these principles to cone deformation, as the amount of the molten material in the cone body increases, the rigidity of the mass becomes less, and the cone gradually softens and bends in the characteristic manner.

Better to understand the cone deformation we might examine Fig. 5, showing the work of Fairchild and Peters.[4] This chart gives us a clear picture of cone deformation and helps us to understand the apparent vagaries of certain cone compositions. The chart is a section from the work of the investigators. The dark areas represent the rate of deformation on slow heating and the light areas the rate of deformation on fast heating. The rate of deformation is normally of little importance, since the cones are standardized for correct end-points; nevertheless some plants fire their ware to a certain cone deformation such as cone 8, one-quarter down. It is therefore helpful to attempt to understand the reasons for the variation in the rate of deformation of the different cones under different heat treatments.

Looking at the chart we might think of the action of the first five cones as normal. That is, they start to deform at a lower temperature when they are heated slowly and are not down until a higher temperature when heated rapidly.

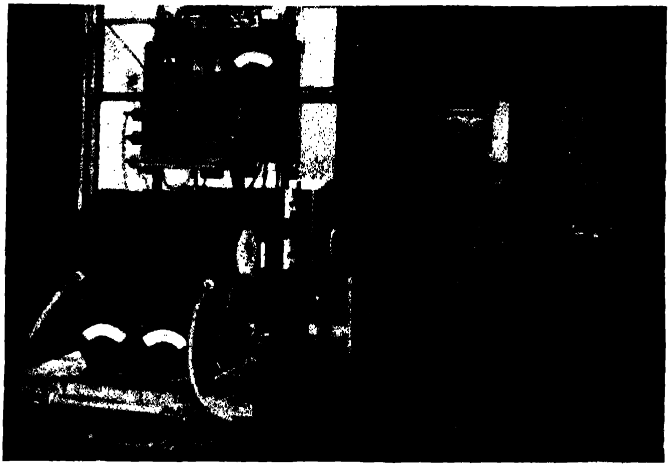


FIG. 6. Electric furnace for standardizing cones.

By way of explaining the action of the cones when heated slowly it would seem logical to assume that a state approaching equilibrium with their thermal environment is being attained. This would mean the maximum amount of reasonably viscous liquids which would account for the slow bending of the cones.

In explaining the action of cone 9 and more particularly of cones 16 and 17, some assumptions must be made. Would it not be reasonable to assume that a considerable amount of a fairly mobile liquid is first formed in the cones, which liquid is hungry for the solid phases? The rapid heating would tend to soften the cone because of the formation of this liquid before it had time to take the solid components into solution. On continued rapid heating the liquid would take these into solution and thereby increase the viscosity and delay the deformation of the cone. The system is now more nearly in equilibrium.

An alternate and more precise explanation of cone deformations may be found in the so-called rim reaction of McCaughey[5] in which the solid phases are said to be surrounded by a reasonably saturated and slow-diffusing liquid phase which forms an interface between the solid components and the continuous phase, which is essentially the superheated eutectic which has sweated out.

Setting the Cones

Cones are set in grogged clay plaques. The plaques may be prefired or they may be of a plastic body. In the fired plaques the cones are set in indentations made before firing. The green plaque material is formed around the cones and dried before being set in the kiln. When the clay is grogged, just what proportion of clay and grog is required has to be worked out by experience, although it is essential that the plaque be more refractory than the cones. The cones and the plaque must shrink to nearly the same degree, for when the plaque shrinks less than the cones the latter become loose and may appear to bend when the real effect is due to shrinkage. The plaques must be dried slowly so as to avoid warping, as a warped plaque can cause the cones to bend erratically.

Certain potteries cast the plaques to the cone base. Casting necessitates a thick casting slip, and the plaque cannot be handled before being dried, else the cones are likely to break off at the base. In placing the cones in the plaque, care must be exercised. A depth mark on the cones suggests a proper depth of imbedding. It is essential that the cones in a plaque be set to this depth in order to insure proper deformation. Straight cones only should be used, as a bent or crooked cone starts to deform before a straight one. Cones warped in the making contain strains in the body which will cause an erratic deformation. Machine-made cones are free from all of these effects. Cones should be inclined to the vertical by an angle of 8°, as specified by the American Society for Testing Materials. This angle should be rigidly adhered to by use of a template. The numbers are usually obscured after deformation, so the cone number should be placed on the plaque immediately below each cone.

Temperature Equivalents

Cones are not temperature-measuring devices in the sense that pyrometers are. They indicate the maturity of ceramic bodies. The value is at times termed "heat-work," meaning a measure of the effect of time and temperature combined.

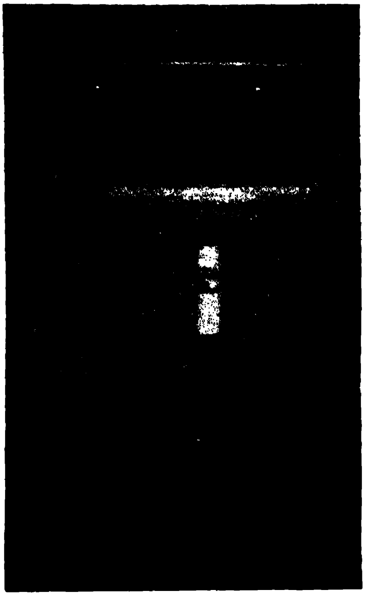


FIG. 7.
Carbon resistance furnace for standardizing high-temperature cones.

Cones measure the degree of maturity of a ceramic body rather than the temperature at which it is matured. They bend slowly as the temperature in the kiln advances or as the ware advances, and they have a definite time-temperature bending interval. For instance, we say that a ceramic body is matured when cone 8 is down.

When cones are advanced in temperature at a given rate they will deform

Table 1. Temperature Equivalents of Cones

Soft Series

Cone Number	When fired slowly 20 °C per hour		When fired rapidly 150 °C per hour	
	(°C)	(°F)	(°C)	(°F)
022	585	1085	605	1121
021	595	1103	615	1139
020	625	1157	650	1202
019	630	1166	660	1220
018	670	1238	720	1328
017	720	1328	770	1418
016	735	1355	795	1463
015	770	1418	805	1481
014	795	1463	830	1526
013	825	1517	860	1580
012	840	1544	875	1607
011	875	1607	905	1661

Low-temperature Series

Cone Number	When fired slowly 20 °C per hour		When fired rapidly 150 °C per hour	
	(°C)	(°F)	(°C)	(°F)
010	890	1634	895	1643
09	930	1706	930	1706
08	945	1733	950	1742
07	975	1787	990	1814
06	1005	1841	1015	1859
05	1030	1886	1040	1904
04	1050	1922	1060	1940
03	1080	1976	1115	2039
02	1095	2003	1125	2057
01	1110	2030	1145	2093

Intermediate-temperature Series

Cone Number	When fired slowly 20 °C per hour		When fired rapidly 150 °C per hour	
	(°C)	(°F)	(°C)	(°F)
1	1125	2057	1160	2120
2	1135	2075	1165	2129
3	1145	2093	1170	2138
4	1165	2129	1190	2174
5	1180	2156	1205	2201
6	1190	2174	1230	2246
7	1210	2210	1250	2282
8	1225	2237	1260	2300
9	1250	2282	1285	2345
10	1260	2300	1305	2381
11	1285	2345	1325	2417
12	1310	2390	1335	2435
13	1350	2462	1350	2462
14	1390	2534	1400	2552
15	1410	2570	1435	2615
16	1450	2642	1465	2669
17	1465	2669	1475	2687
18	1485	2705	1490	2714
19	1515	2759	1520	2768
20	1520	2768	1530	2786

at or near a given temperature. The National Bureau of Standards has studied the "Standard Cones" on two different heat schedules. The cones were heated 150 °C per hour and at 20 °C per hour with the following results:

As indicated previously, when cones are heated at different rates they will deform at different temperatures. Investigators in the U. S. Bureau of Mines[6]

Table 1.—(*Continued*)

High-temperature Series

Cone Number	When heated at 100° per hour (°C)	(°F)
23	1580	2876
26	1595	2903
27	1605	2921
28	1615	2939
29	1640	2984
30	1650	3002
31	1680	3056
32	1700	3092
32½	1725	3137
33	1745	3173
34	1760	3200
35	1785	3245
36	1810	3290
37	1820	3308
38	1835	3335
*39	1865	3389
40	1885	3425
41	1970	3578
42	2015	3659

* The last four cones were heated 600° per hour.

found that the cones went down at temperatures much lower than those reported by the National Bureau of Standards. They were firing silica brick on a 15-day schedule. The temperatures at which the cones deformed in a fire-brick kiln, when fired on a seven-day schedule, were much nearer the temperatures on the National Bureau of Standards' slow schedule, but were still decidedly lower.

Cones are often used to determine the uniformity of the heat distribution in ceramic kilns. For this purpose the cones are usually placed inside the saggers in the potter's kiln or "blind" in a brick kiln. They are placed at different levels in the kiln and at different cross-sections. They indicate changes in drafting or even in kiln design which will equalize the heat.

We can but repeat that cones are not pyrometers and should not be so used. Thermocouples should always be kept in the top and, where possible, in the bottom of the kiln to indicate the temperature and to enable the fireman to keep a constant temperature schedule. Cones, however, measure ware maturity in an accurate manner and in a way that can be compared from plant to plant.

* * * * *

Discussion of this paper has been combined with that of the succeeding paper and follows the latter.

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Temperature Measurements in Ceramics

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A ceramic temperature scale is an indirect scale based on the variation with temperature of some property of a clay or of a ceramic mixture. The two properties which have been most utilized are shrinkage and fusibility. The former is the basis of the "Veritas" ring system. Any clay exhibits a characteristic shrinkage curve when fired on a definite heating schedule. The shrinkage can therefore be correlated with temperature. The disadvantage of this system lies in the fact that the ring or bar must be removed from the kiln and allowed to cool before measurement can be made. The advantage lies in the broad temperature range covered by shrinkage, so that a single clay may be all that is needed for control.

The system of pyrometric cones more generally used is based on the preparation of a series of ceramic mixtures of successively decreasing fusibility, so devised that the entire working temperature range is covered. Each mixture exhibits a softening range rather than a sharp melting point, so that the cone-shaped specimen covers a more or less definite range of temperature in falling from the upright to the bent position. Usually, this interval is about 20 °C and the original cone scale devised by Seger is based on such steps. Seger determined the most fusible mixture of feldspar, whiting, quartz, and kaolin, which had the following R O composition:

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} 0.5\ Al_2O_3 \cdot 4\ SiO_2$$

This became Cone 4 in his series. Lower cones were made by adding iron oxide and higher cones by increasing the quartz and clay content. From No. 28 up, the cones consist only of mixtures of quartz and kaolin. Following Seger's work, the series was extended so that we now have a soft series from 585° to 1110 °C (022 to 01); an intermediate series from 1125 to 1520 °C (1 to 20); and a high series from 1580 to 2015 °C (23 to 42). It is not the present purpose to consider the development and improvement of such a cone series, but rather to discuss the ultilization of cones and their relationship to other methods of temperature control.

Historically, pyrometric cones were introduced at a time when other methods of temperature measurement were not available to the ceramic industry. With the development of the more sensitive thermoelectric, radiation, and optical pyrometry, it might be supposed that the ceramic method would have become obsolete. The newer methods have been applied in conjunction with cones, but not to replace them. The cones have persisted because of their convenience and simplicity, because an unlimited number may be used to indicate conditions in all parts of a large kiln, and because they can be placed so as to register the condition of the work and not merely the temperature at some arbitrary point in the kiln. These practical considerations are of particular importance in the ceramic industry because of the nature of the products and processes, as will appear in later discussion.

To the foregoing summary of the peculiar utility of cones, many would add the statement that cones do not measure temperature at all but serve directly to indicate "heat work," *i. e.*, the actual progress of development of the ware being fired.

Such a concept may be valid under very special circumstances, but a little consideration will show that it cannot be generally true.

It is well known that both time and temperature influence the deformation of cones. Thus cone 10, which according to the early tables deforms at 1330 °C, has been found by the Bureau of Standards to come down at 1305 °C on a heating schedule of 150° per hour rise, and at 1260° on a schedule of 20° per hour rise. In industrial kilns it may come down as low as 1230°. It is true that all ceramic products exhibit an analogous behavior. In respect to many physical properties equivalent results may be obtained at a high temperature for a short time, or at a low temperature for a longer time. But it will be obvious that we are here dealing with questions of thermal capacity involving mass, specific heat, and thermal conductivity of the object being fired. Only in the special case where these properties coincide for work and cone can the latter correctly reveal the conditions of the former.

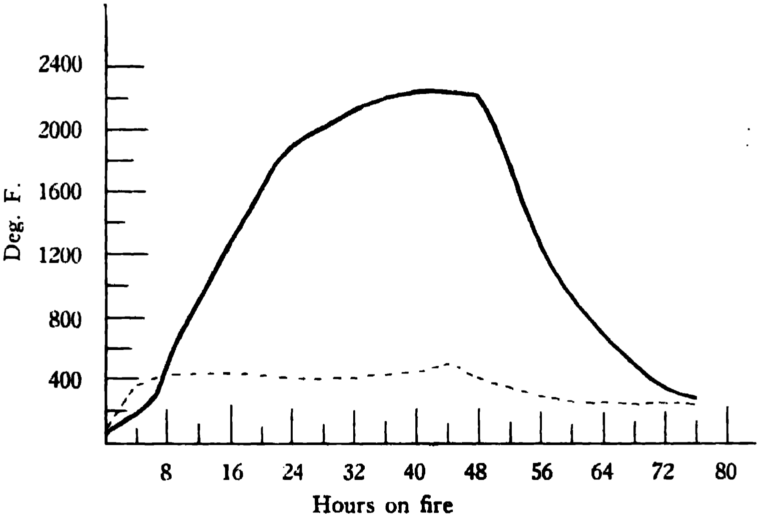

FIG. 1. Tunnel kiln firing electrical porcelain.

Of the three properties mentioned, mass is the chief variable and the determining factor in heat treatment. With products ranging in size from spark plugs to bath-room fixtures, from small crucibles to tank blocks and grinding wheels, there can be no universal indicator to give the end point of heat treatment.

These difficulties in the interpretation of cone deformations disappear when the cones are used in conjunction with a thermocouple control system and the kiln is operated on a definite heating schedule. Under these circumstances, as was shown by Fairchild and Peters in a study at the Bureau of Standards, the cones deform at commercially definite temperatures and can be regarded simply as devices for measuring temperature. It is of no consequence whether or not these temperatures agree with those recorded in tables. The pyrometer system, instead of displacing cones, has enhanced their usefulness.

If it is necessary to fire with cones alone, an effort should still be made to observe a definite time-temperature cycle. This is accomplished by bringing down the cones, not arbitrarily, but at stated intervals and in as uniform a manner as possible, thus establishing the necessary control of the heating schedule.

Temperature measurement is only one of the elements in industrial heating operations. In ceramics we have to deal with products having very low thermal conductivity, high specific heat, and sometimes large masses. In addition there occur a number of exothermic and endothermic reactions, notably the dehydration of clay, oxidation of carbon and sulfur, decomposition of carbonates, and recrystallization into new forms of various silicates. There is the further necessity of considering the reversible expansion and the permanent shrinkage of clay wares under fire. This shrinkage may amount to one-third the original volume, yet contours must be preserved without distortion. It is not surprising that long periods of time are required for successful heat treatment, and that such matters as rate of heating, time of soak, circulation of gases, method of heat transfer, and manner of cooling, assume the same importance as temperature control. The time cycle may range from 12 hours for firing dinnerware in a decorating kiln to 200 hours for firing large grinding wheels. By way of illustration several curves are given.

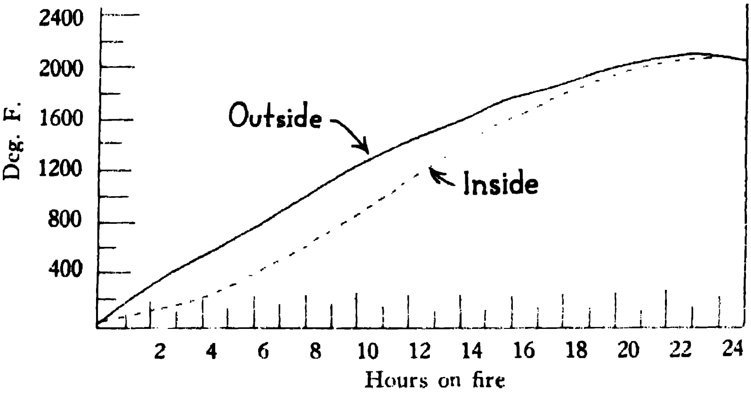

FIG. 2. Fast periodic kiln fire. Temperatures outside and inside sagger.

(1) Firing Curve of a Biscuit Tunnel Kiln.

This curve represents readings obtained with a test car moving through a tunnel kiln, equipped with platinum-rhodium couple and long copper leads, and a long base-metal couple to record the cold junction temperature of the platinum couple.

(2) Temperatures Inside and Outside a Sagger.

These curves were obtained by thermocouples in a regular large periodic kiln. They illustrate the significance of temperature lag due to the refractory container and bring out one of the essential advantages of cones. These are placed inside the container where they are subject to the same conditions as the work.

(3) Curves Showing the Temperatures on the Outside and Inside of a Ceramic Product 9" in Diameter and 8" High During the Heating Period.

Note the large lag of the center couple and the break in the center curve which registers the heat absorption in dehydrating clay.

It will be obvious that the type and construction of the kiln have a great deal to do with the method of temperature control. Periodic kilns can be equipped with a single thermocouple for general control of the heating rate, but this is inadequate to cover all parts of the kiln. Cone bats are placed in saggers with a cut-out wall where they can be sighted through peep holes. Such cones are the chief reliance in firing off these kilns. They may be supplemented effectively by the use of optical pyrometers. In addition to the control "sight" cones, it is customary to place throughout the kiln numbers of "blind" cones, which are of no help in firing but serve as a check-back at the end of the operation.

In tunnel kilns, the moderate cross-section makes it possible to secure greater uniformity in the hot zone than is possible throughout the mass of a periodic kiln. It is quite possible to control such kilns by means of thermocouples, and gas- or oil-fired kilns are commonly equipped with automatic controls actuated by couples in the high fire zones. Even here, it is good practice to use blind cones as a means of covering the entire section of the kiln and to serve as a guard against any difficulty with the pyrometer control system. Rare-metal couples have a limited life in tunnel kiln operation. When the kiln is built it is desirable to provide double thermocouple openings so that working couples can be easily checked in place against a standard.

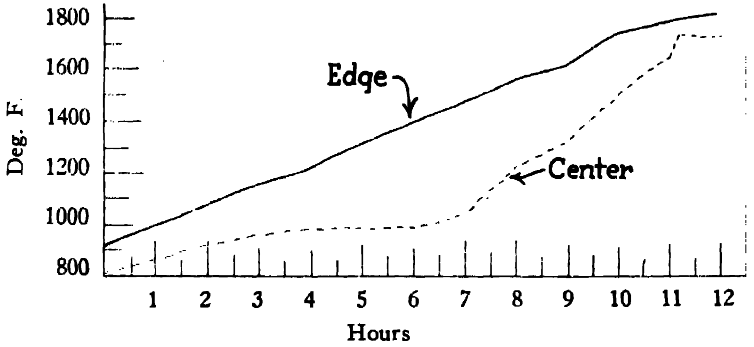

FIG. 3. Temperatures edge and center of clay ware 9 in diameter.

Discussion

G. A. Bole: Several points in Dr. Schramm's paper on temperature measurements in ceramics deserve emphasis. Although definite temperatures are tabulated in the literature for pyrometric cones, definite temperatures are not indicated by these cones unless they are heated under prescribed conditions. A laboratory furnace can be operated under such conditions that the cones come down at definite temperatures, but an industrial ceramic kiln is rarely so operated. In the industry, therefore, we cannot claim that pyrometric cones indicate definite temperatures.

It happens, however, that definite temperatures are not very important in the industrial firing of ceramic ware. Physical and chemical reactions between the various ingredients of these complex mixtures are involved in this process, and it is further complicated by the fact that these reactions must be halted at various stages of their progress in order to impart to the wide variety of ceramic wares the great number of different properties which they must have. This means that something other than mere heating to a definite temperature is required.

C. O. Fairchild: In discussing these two papers by authorities on the manufacture and use of cones, the first thought that comes to mind is that satisfactory pyrometers have been used in the ceramic industry for many years, and that the time has passed when there could be any argument about whether cones should be displaced by pyrometers for the control of the heat treatment of clay wares. Their complementary functions have been ably discussed by both authors, and

Dr. Schramm has emphasized not only the principal reasons for the universal use of cones, but also the particular case of firing very large masses which may require a soaking period. If cones are being used to help in the firing of 200-pound grinding wheels, and we may assume that they are, then it would appear that Dr. Bole need not be concerned about the continued use of cones in the future, nor feel the necessity of arguing that cones measure something like "heat work," and can do this successfully because they are similar to the ware. I mean to say that since cones and pyrometers have been used in conjunction for so many years, it seems unnecessary to argue any more about why cones should be used. Certainly the American Ceramic Society, in establishing the Edward Orton Jr. Ceramic Foundation, and placing Dr. Bole in charge, had concluded that cones will always be used.

Dr. Bole's statement that in making cones the batches are corrected until test cones behave identically with corresponding standard cones, both in a gas-fired kiln and an electric furnace, deserves particular attention. The conclusion is that no observable differences are permitted. Perhaps this explains in part why ceramists continue through the years to retain an extraordinary degree of confidence in pyrometric cones.

If Dr. Schramm agrees that cones *may properly* "be regarded simply as devices for measuring temperature" while a definite heating schedule is followed, then his expression "ceramic temperature scale," as applied to cones, is open to some objection. "P. C. E.," adopted by the American Society for Testing Materials, avoids this objection and the possibility of some confusion. I would like to think of a cone as an "on schedule" indicator, if only one variable, namely, departure from the predetermined schedule, is to be included in the descriptive expression, instead of the two variables, time and temperature. Of course, as an "on schedule" indicator, the cone is peculiar in that it is much more sensitive to positive temperature departures from the schedule than it is to negative departures and cannot reverse its response—hence the pyrometer for maintaining the schedule.

Reply

From the discussion it is clear that all are agreed that temperature measurements alone, by whatever means obtained, are only one factor in the control of heat treatment. Other factors are the manner of setting the kilns, the circulation of gases and, above all, the time schedule or heating rate. The writer's position is simply that no cone or other device can properly measure two things at once. There is no lack of instruments for measuring and recording time, and the true function of cones is to serve as auxiliary temperature indicators. The conditions which make this possible can now be realized because of advances in the art of building and operating kilns. As an example of the uncertainties in the "heat work" theory of cones some recent observations by Connor on brick kilns may be cited. In different parts of the setting the same cone deformation accompanied a wide range of porosities in the brick, and conversely, the same properties in the brick were obtained with entirely different cone deformations.

Chapter 11

Oil Industries

Problems of Temperature Measurement Concerning Petroleum Production

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In order to appreciate the utility of measuring transitional temperatures in boreholes it is necessary to be generally familiar with a typical procedure of drilling and completing an oil well. At the present time, the great majority of wells are drilled with rotary equipment in which, during drilling, mud is circulated through the rotating drill pipe past the cutting edge of the bit, and up through the annular space between the drill stem and open hole. This mud is chosen to be sufficiently viscous to carry the formation cuttings to the surface, and is of sufficiently high specific gravity that its hydrostatic pressure at any point is not exceeded by the pressure in the earth formations which are likely to be encountered. This prevents the well from producing prematurely, and reduces caving of poorly consolidated formations.

After the hole has been drilled through the unconsolidated upper layers and shallow water sands, the first string of casing is set. In the Gulf Coast, this may be anywhere from a few hundred to a thousand feet deep. When this pipe is in position, cement is pumped through it, and fills the lower part of the annular space between its outer wall and the earth by displacing the mud from the bottom. After this cement has set, drilling is resumed in the same manner with a smaller bit than was previously used, and is continued through the shale, water-sand and rock formations, into the oil-bearing strata. In order to know the point at which drilling should be stopped and the manner in which the well should be completed, one must know the nature and extent of the oil-bearing reservoir.

Most Gulf Coast oil-sand bodies are streaked with irregular shale sections and have lying above them similar sands containing gas, and below them sands containing salt water. If the well is completed at too shallow a depth, the ratio of gas to oil produced will be unnecessarily high, with the result that reservoir pressure will be lost and ultimate recovery reduced. If the completion depth is too great, salt water will be produced. This optimum point is generally determined with varying degrees of certainty by means of earth sampling devices, electric logs, and past experience in near-by wells. Drilling is stopped at a depth which is supposed to be a safe distance above the water bearing section. An oil string of casing is then suspended below the gas bearing section and is cemented into position. Enough cement is pumped in through the casing to the annular space behind the pipe to seal the oil sand from other formations. After the cement has set, the plug of cement remaining in the bottom of the casing is drilled out, and a string of tubing is run inside the casing from the surface to the producing horizon. Suitable connections and valves are arranged at the surface, and the well is brought into production by circulating clear water through the tubing and casing. This water displaces the heavy mud used for drilling, thus reducing the hydrostatic pressure of the well fluid until it is exceeded by the fluid pressure in the oil sand. When sufficient fluid pressure exists, the flow becomes spontaneous and is controlled by valves at the surface.

After the well has flowed enough to clean itself of the remaining mud and

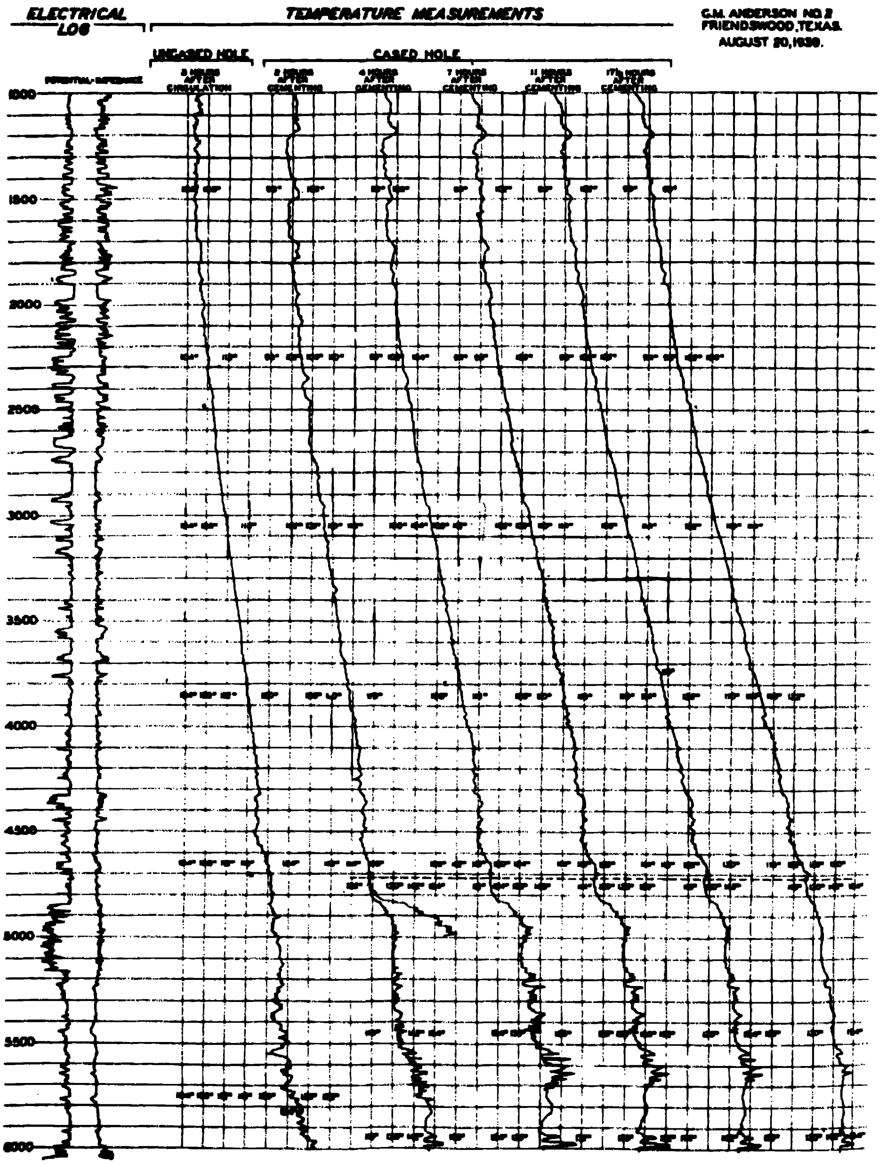


FIG. 1. Comparison of temperature measurements with electrical log.

water, the oil is turned into storage tanks. Production is continued in this manner unless the well begins to produce an abnormal amount of gas or water. This may be due to the completion depth having been too low or too high, to faulty cementing of the oil string or to a leak in the casing, or simply to depletion of the available oil. If the cause is known, however, the procedure of reworking the well is determined.

The answer to a number of questions which arise between the time drilling is started and the time the well is abandoned may be determined by observing a continuously recorded log of temperature vs. depth, made under suitable conditions.

The first stage in this procedure at which a temperature survey is useful is in the open hole after drilling has been completed. First, the drilling fluid is circulated for an hour or more, until its temperature gradient is fairly uniform throughout the mud column. In the upper part of the hole this fluid temperature is generally higher than that of the surrounding earth, and in the lower part is correspondingly lower. At some intermediate point, the fluid and earth are in thermal equilibrium. The drill pipe is then removed and the hole is left idle for about three hours, after which time the survey is made. In the upper and lower parts of the well, where the fluid is at a temperature different from that of the surrounding earth, there will be a flow of heat between the earth strata and the well fluid. At any point in the well the quantity of heat flowing to or from the well fluid is a function of the temperature difference between the earth and fluid, and of the thermal conductivity of the surrounding earth material. Differences in the conductivity of the various earth strata cause corresponding variations in the recorded temperature. In permeable sections, invasion of the well fluid also affects the temperature. As shown in Figs. 1 and 2, these variations are greatest near the top and bottom of the well and become very small near the center.

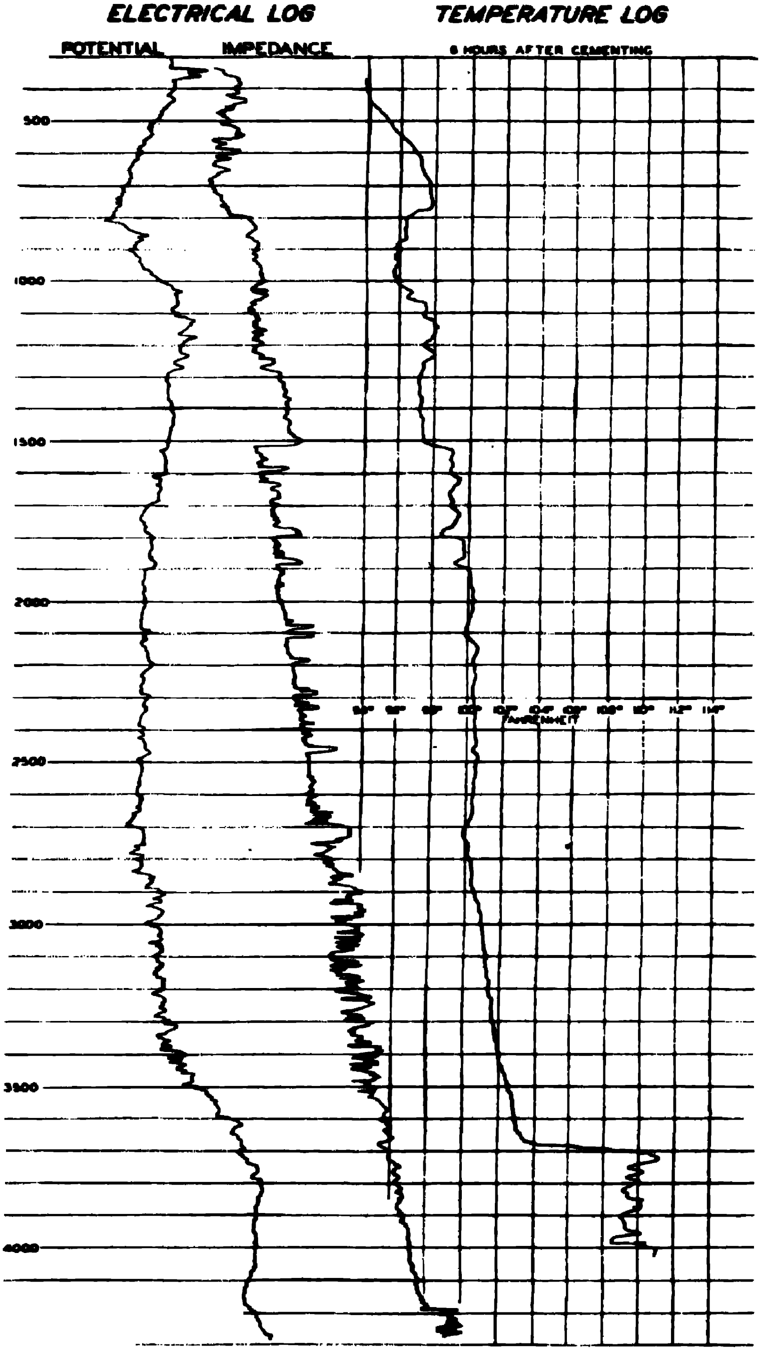
In regions where the earth strata are mainly made up of hard rocks, such as limestone and sandstone, these temperature anomalies have corresponding anomalies shown in a similarly recorded log of electrical measurements made in the open hole. In many instances, however, anomalies of high resistivity in the electric log correspond to anomalies of high thermal conductivity in the temperature log. Earth strata made up mainly of sands and shales, such as occur in the Gulf Coast, generally show no obvious correlation between electric and temperature logs.

After the oil string of casing has been put in place and cemented, a temperature survey similar to the one previously described shows anomalies associated with the thermal conductivity of the earth strata which are similar to those seen in the open-hole log, although somewhat less sharp. Fig. 2 shows a cased-hole temperature log made in West Texas in which good correlation exists between the temperature log and an open-hole electric log.

The cased-hole log also indicates clearly the extent of the cement behind the casing. As was pointed out in the introduction, the purpose of this cementing is to seal the overlying strata containing gas or water from the oil-bearing horizon which is to be produced. If unknown cavities exist in this region, the computed volume of cement may not be sufficient to effect the desired seal. During the setting of the cement, sufficient heat may be liberated to raise the temperature of the well fluid by as much as 50 °F. The series of logs shown in Fig. 1 indicates that the maximum temperature of this region is reached about four hours after cementing.

It is interesting to note in the series of logs shown in Fig. 1 that the temperature opposite the oil-sand shown in the electric log to be at 5990 feet is 18 °F cooler than that opposite the shale section immediately above. The reason for this is not known.

When a producing well, either initially or at some later time in its life, yields a much higher ratio of gas or water to oil than is reasonably expected, temperature logs may be used to determine the cause of this misbehavior. To locate the point of influx of gas it is preferable to run the thermometer under pressure through a packing gland in the inside of the tubing, and to produce the well through the casing. The point at which gas enters the well will be characterized by an anomaly of decreased temperature due to the cooling of the well fluid by the expanding gas.



C. SCHARBAUER NO. B-4 GOLDSMITH FIELD, TEXAS.

FIG. 2.

Its magnitude may be controlled by varying the rate of production of the well. If this point of entry is found to be in the cased part of the hole, a leak in the casing is known to exist. If it coincides with the lower end of the casing the fault is a bad cement seal above the oil-sand. Fig. 3 shows such a log. Either may be corrected by squeezing cement into the leak. If the gas is found to be entering in the open section at the bottom of the hole, it is an indication either that the casing has been set too high or that the oil is depleted. The location of the point of influx of water is somewhat more difficult, in that the well fluid must first be brought to some temperature different from that of the water which is flowing in.

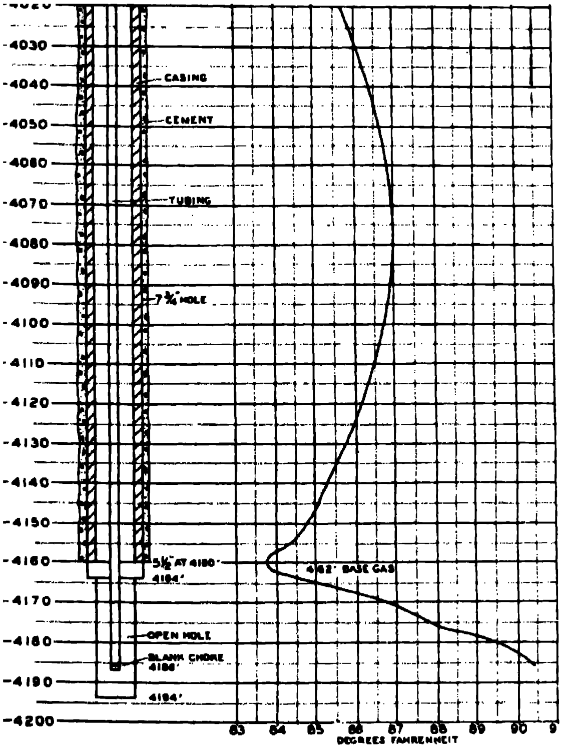


FIG. 3.

This may be accomplished by circulating the well fluid as was done in the open hole. If the leak happens to be near that part of the well which is in thermal equilibrium with the surrounding earth, it may be necessary to heat or cool the circulated fluid artificially in order to obtain reliable data.

The requirements of a thermometer for obtaining these data are specialized and in some respects rather rigorous. Measurements made at isolated points are obviously of little value; all should be made continuously as a function of the depth of the hole. The depth determinations are much more precise and the construction is greatly simplified if the recording is done at the surface rather than in the instrument in the hole. Particularly in surveys made in open holes, the speed at which the instrument may be run is an important factor because of the expense of idle time for the drilling crew and equipment, and the hazards of leaving the hole open an unnecessarily long time. In all instances it is desirable that the indicated temperature be as close to the actual temperature of the fluid being measured as possible. From these considerations, the thermal capacity of the measuring element should be kept small, and there should be a minimum of insulating material between the element and surrounding fluid. The sensitivity and range of the instrument must be readily variable in order to accommodate the wide range of conditions encountered in different wells and even at different depths in the same well. Experience has indicated that the range of temperatures encountered is from 80 to 250 °F. The recording sensitivity should be variable in several steps from about 4 to 24 °F per inch. It is obviously impractical to employ a recording chart of sufficient width to accommodate this range; consequently, the galvanometer must be reset by a known amount whenever the image approaches the edge of the strip.

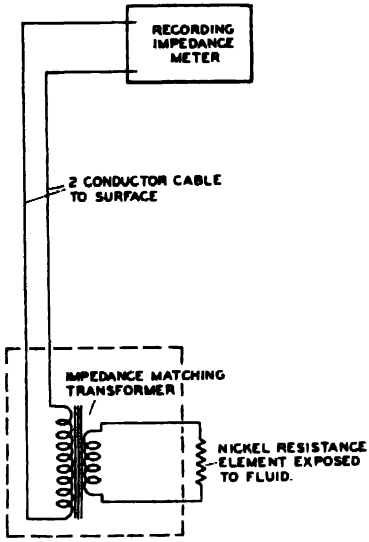

RECORDING IMPEDANCE METER
2 CONDUCTOR CABLE TO SURFACE
IMPEDANCE MATCHING TRANSFORMER
NICKEL RESISTANCE ELEMENT EXPOSED TO FLUID.

FIG. 4.

The resulting "saw tooth" record must then be retraced in order to obtain a continuous curve of temperature vs. depth. In use, the whole instrument should be able to withstand rather rough treatment; for example, the indicated temperature must not be changed when it strikes hard, protruding ledges in the walls of the hole.

These considerations have led to the general use of electrical resistance thermometers. The element, together with the insulated two-conductor cable to the surface, forms the variable arm of a Wheatstone bridge. However, conductor cables which are practicable from other considerations are made of copper, whose temperature coefficient of resistivity is high, and usually have a resistance of from one to two hundred ohms; consequently the measuring element should have a resistance of several thousand ohms. Since the fluids whose temperature is measured vary widely in resistivity, it is essential that the electrical circuit be well insulated from the well fluid. Due to the abrasive action of this fluid, it is not possible to maintain the thin coating of insulating material on the measuring element which is desirable; consequently, the time required for the element to reach thermal equilibrium seriously limits the speed at which the survey may be run.

These limitations have led to the development of a modified form of resistance thermometer in which the measuring element is exposed to the fluid in the well with no electrical insulation between them. This is accomplished by using an element whose resistance is small compared to the shunt resistance contributed by the drilling fluid. The first successful instrument of this type employed a transformer near the measuring element, with the low-impedance primary winding connected to the element and the high-impedance secondary connected to the line and measuring circuit as shown in Fig. 4. The usefulness of this arrangement was limited, however, by a slow drift of the indicated temperature which was caused by the gradual heating of the transformer. This seriously limited the precision with which the actual temperature could be measured, although its speed, range and sensitivity were satisfactory.

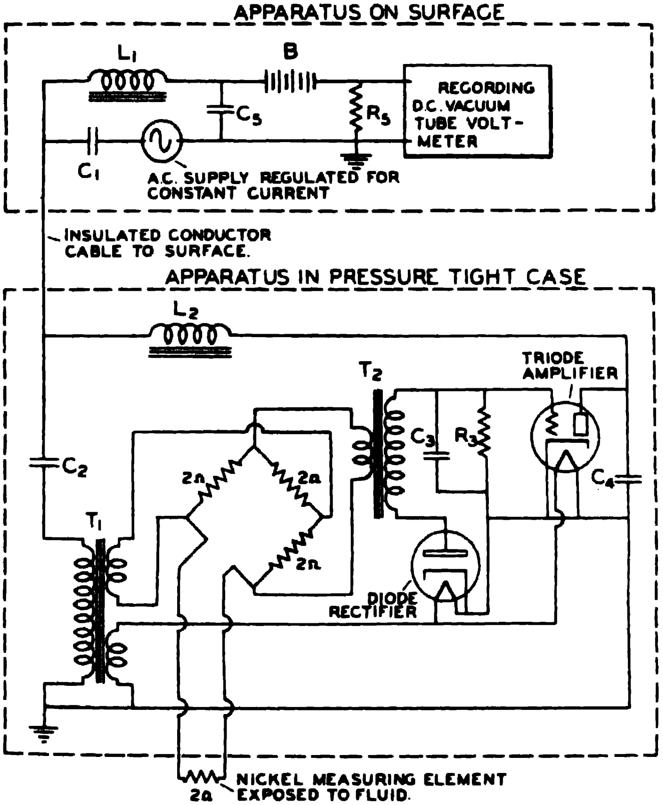

APPARATUS ON SURFACE
L₁
B
C₅
R₅
RECORDING D.C. VACUUM TUBE VOLT-METER
C₁
A.C. SUPPLY REGULATED FOR CONSTANT CURRENT
INSULATED CONDUCTOR CABLE TO SURFACE.
APPARATUS IN PRESSURE TIGHT CASE
L₂
T₂
TRIODE AMPLIFIER
C₃
R₃
C₂
2Ω
2Ω
C₄
T₁
2Ω
DIODE RECTIFIER
NICKEL MEASURING ELEMENT EXPOSED TO FLUID.
2Ω

FIG. 5.

A later modification, shown in Fig. 5, does not have these limitations. A similar measuring element is used which, together with three resistance elements of constantan, form a low-resistance Wheatstone bridge. A. C. current is supplied through condensers C_1 and C_2 and the cable to the bridge by transformer T_1. The off-balance voltage is impressed on the primary of transformer T_2. The high-impedance secondary is connected to a diode rectifier which converts the A. C. voltage to a D. C. voltage appearing across R_3 and the grid circuit of the triode.

Plate voltage for the triode is supplied by a battery, B, through plate resistance, R_5, inductances L_1 and L_2, and the insulated conductor cable. Hence the voltage appearing across R_5 which is recorded is determined by the temperature of the measuring element. The sensitivity is about 50 mv per °F.

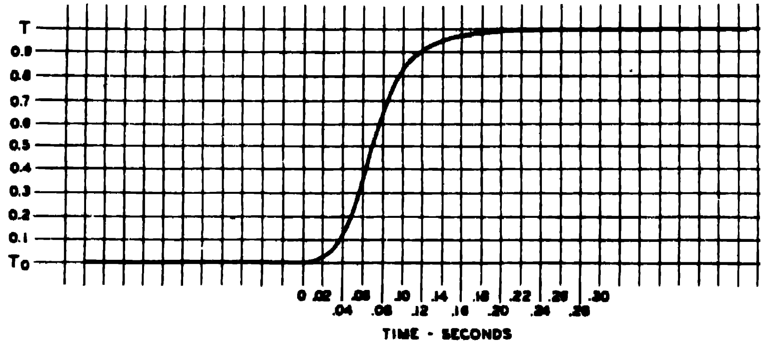


FIG. 6. Thermometer plunged into water at temperature T from air at temperature T_0.

Fig. 6 shows an oscillogram of the measured temperature vs. time when the element was plunged from air at temperature T_0 into water at temperature T. Errors due to variation in the A. C. supply current are proportional to the difference between the temperature being measured and the temperature at which the bridge is balanced. In practice, this current is held constant to .5 per cent.

Although this arrangement is somewhat more complex electrically than is desired, its performance in the field has been quite satisfactory. It is believed that the saving in time of operation will make it possible to run surveys on more wells than has been practicable in the past, and that these additional data will lead to a clearer understanding of the significance of the anomalies than exists at the present time.

Thermal Prospecting for Oil

M. C. Terry and J. H. Burney
Humble Oil & Refining Co., Houston, Texas

Any sort of geological structure which involves some porous material sealed from above may prove to be oil-bearing. For example, oil is often found where the beds are concave downward due to folding or the intrusion from below of salt or igneous plugs. Frequently too, porous formations are sealed properly by faulting. It is indeed fortunate that many of these structures can be detected by surface measurements without drilling a well. Among the standard methods of approach to the problem of finding structures there are three of sufficient interest to the physicist to be discussed briefly here. The most important of these is seismology, which takes advantage of the fact that the impulse from a dynamite explosion is reflected from some beds. Depth to the bed is computed from the time interval between the explosion and the arrival of the reflected impulse at the surface. Also, very accurate determinations of g or grad g may reveal buried structures because very often the material of the structure has a density sufficiently different from that surrounding it to affect the acceleration of gravity at the surface. The third method involves a search for anomalies in the earth's magnetic field, which may be due to intrusion or distortion of magnetic material.

Van Orstrand and various workers sponsored by the American Petroleum Institute have built up a large body of data from temperature measurements taken at considerable depths in inactive oil wells which shows that ground temperatures are measurably higher over some oil-producing structures. In some cases, it is even possible to draw contour maps from their thermal data that are in remarkable agreement with those based on the findings of the drill.

Since this technic is obviously impractical for prospecting, we substituted resistance-thermometer coils buried in small core holes drilled with a light rig mounted on a truck. The coils were suspended two to a hole, at 100 and 200 feet, on a three-conductor rubber-covered cable, which also served for leads. The coils were threaded on a cable and covered with a length of rubber tubing, the ends of which were vulcanized to the cable cover.

The thermal coefficient of resistance was determined for the particular brand of wire used by measurement in an ice bath and in a bath maintained thermostatically at 32.92 °C. After it was established that the resistance coefficient did not vary materially from batch to batch of wire, the ice bath was dispensed with in calibration. The coils normally had a resistance of about 500 ohms which was measured with a portable Wheatstone bridge using fixed steps down to tenths. The galvanometer was sensitive enough to permit estimation of quarters of the smallest step. Thus measurements were accurate to less than 0.02 ° C, which seemed to be about the limit of equilibrium in the ground under the best circumstances. Since, in general, uncased holes in the type of material encountered cave-in a short time after drilling, the measurements should be truly indicative of ground temperature. From four to six weeks is required to establish thermal equilibrium after drilling. In some cases equilibrium never did seem to be established, which fact is probably due to circulation of ground water.

So far, two profiles have been surveyed, one in the South Texas area and one from the middle of the Hastings field across the Friendswood field near Houston. The South Texas survey showed nothing in particular except a dip of the isothermal surfaces parallel to that of the beds in that region. There are no other data available on the area except those of the core drill, which shows no indication of structure. There is no reason to suspect the existence of a structure. The Hastings-Friendswood profile showed 0.8 °C rise over Hastings and 0.7 °C over Friendswood. The peak over Friendswood is very flat and a mile and a half wide, and corresponds fairly well to the limits of production. On the side away from Hastings it falls off very rapidly and flattens out within a mile. The limit of production has not been definitely established on this side of the field, but a dry hole has been drilled within a few hundred yards of the point where the profile breaks. Of the seventeen cables placed at half-mile intervals on this profile, ten gave data which fitted a smooth curve while that from the rest did not. However, the data that did not fit could, in every case, be thrown out on the basis of poor equilibrium, while the rest fit the curve perfectly. Since the driller found evidence of water sands in many of the holes, we feel that lack of equilibrium indicated that the coils were exposed to migrating water, while where equilibrium was established the water either was not present or did not move. This may not be the true reason for failure of the coils to show thermal equilibrium, but it seems a likely explanation. In any event, we feel the failure to maintain equilibrium to be a valid reason for eliminating these points from consideration, and the fact that the temperatures we did use have persisted for six weeks is proof of their reliability. This profile has been extended on each end, but, unfortunately, the coils have not been in place long enough to use the results.

A possible objection to the validity of our results is that a producing oil field is not in an undisturbed thermal condition, *i.e.*, there is considerable heat generated by the friction of the drill, drilling mud is pumped down the drill stem and back up the hole to wash out the cuttings, thus heating the upper formations by exchange with the warmer rocks at the bottom and by friction on the sides. Also, the oil produced might heat the surface formations by exchange. However, the following simple calculation shows the effect must be negligible.

To September 1, Friendswood produced 2,580,645 barrels of oil from 172 wells, an average of about 15,000 barrels or 1.79×10^9 cm^3 per well. In place, this oil is at about 68 °C, has a specific heat of about 0.511 calorie per gram and specific gravity 0.88. If we assume it is cooled to the surface temperature of 22 °C it will then give up 5.8×10^{10} calories. On the average, it takes about 5 days' actual digging to drill a well in Friendswood, which means that not more than 1000 horsepower is applied for this time. This is equivalent to 8.05×10^9 calories, and we shall assume that all the energy goes to overcome friction of the drill and the circulating mud. If we assume further that all the mud goes to bottom hole temperature and back to surface temperature at each circuit of the hole and makes three round trips an hour for five days, we have 4.74×10^{11} calories dissipated. The total available then is 5.4×10^{11} calories.

Wells are spaced one to 20 acres in Friendswood and are 5800 feet deep, on the average. If we assume all the heat to be dissipated in the upper third of the surrounding formation, 40,000 acre-feet of earth will be warmed. This is a volume of 4.96×10^{13} cm^3 and has a mass of 1.24×10^{14} grams, assuming a density of 2.5. The specific heat being about 0.22 calorie per gram, the total heat capacity of this mass is 2.73×10^{13} calories. Thus, even in the highly improbable event of all the heat from all available sources being transferred without loss to the upper third of the hole, the temperature rise would be less than 0.02 °C. Even if this heat affected only the region in which our measurements were taken, that is the top

200 feet, the effect would result in a rise of only 0.2 °C, which is still considerably less than the observed rise of 0.7 °C. Thus, apparently, the only reason to doubt that we have here a workable method of prospecting is the possibility that the effect is due to some other unrelated cause as yet unexplained, and that the positive indication on two known fields and negative results where they were to be expected in South Texas, together with the data collected by others, are purely coincidence. Because of the scarcity of information as to just what is taking place more than ten thousand feet below the surface of the earth, any explanation of this phenomenon lies somewhere on the shaky ground between theory and speculation. Hence, coincidence cannot be refuted, but merely made more improbable by further work.

We have no theory of our own to propose or time to discuss more than a few of those advanced by others. It has been suggested that oxidation of the oil might account for the temperature rise. This would be very fortunate indeed, because we would then have the long sought-after method that finds oil itself rather than structure, and hence could find the structureless traps like East Texas. However, surveys on such fields show little thermal anomaly; oil sands are no warmer than other formations at the same depth; and Van Orstrand has shown by a simple computation involving the heat of combustion of petroleum that, if this were the explanation, the oil in the fields he surveyed would all have been consumed long since if the reservoirs are anywhere near as old as the geologists say they are.

Probably the most plausible explanation for our results is that Hastings and Friendswood are thought to be on top of deeply buried salt domes. Now salt has a considerably higher conductivity than the ordinary sediments of the Gulf Coast, and there is known to be an increase of temperature with depth. The source of this heat is still in some doubt, but the only one available in the surface rocks with which we are familiar is radioactivity, and there is a higher concentration of radioactive substance in igneous than in sedimentary rock. Since in the Gulf Coast there are 25,000 feet or more of sediments on granite, the center of gravity of the source of this internal heat is at considerable depth, and the heat resistance of the path from it to the surface is considerably less over the fields, where a goodly portion of it is in salt, than where it is entirely through sediments. Thus, we would expect the higher temperature over the field.

The fact that the isothermals in South Texas seem to follow the regional dip is harder to explain. It has been suggested that heat conductivity along the planes of the interfaces of the beds may be more than across them, and that ground waters circulating upward would tend to move parallel to these interfaces rather than across them is also possible; both these factors would make for an increase in temperture up-dip.

The profile obtained does not tell as much as the reflection seismograph, but it is a more positive indication than that obtainable by gravimetric means. Its operation is cheaper than the seismograph but more expensive than the gravity meter. The initial outlay for equipment is considerably less than required for either of the other methods, and the apparatus requires less maintenance. Thus it would probably be most useful for reconnaissance, and might be of great importance in territory where good reflections cannot be found.

Temperature of the Earth in Relation to Oil Location

C. E. VAN ORSTRAND
Geological Survey, Washington, D. C.

Introduction

Nearly 200 years have elapsed since Gesanne in 1740 made observations of temperatures in the mines of Alsace. From the earliest observations to the present day, all the reliable observations show clearly that the temperatures in the earth increase with depth. It is a curious and interesting fact that the explanation of this simple phenomenon leads us on the one hand into profound speculations concerning the origin of the solar system and on the other hand to theoretical and practical applications that are of fundamental importance to the geologist and petroleum engineer.

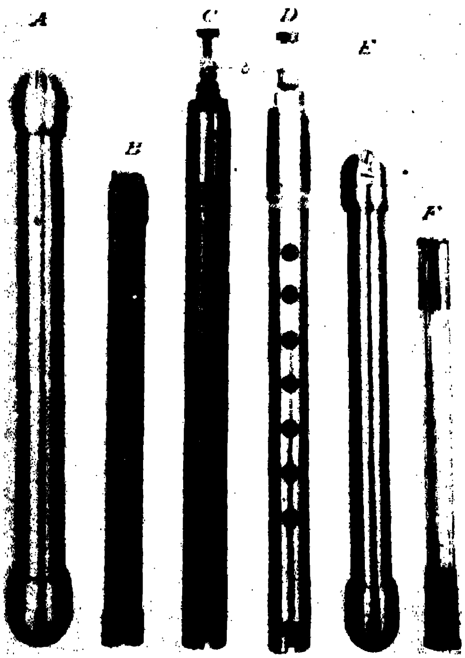


FIG. 1.

Tubes for lowering maximum thermometers into deep wells.

Methods of Measurement

Maximum Thermometer. In 1869, Lord Kelvin observed the temperatures to a depth of 347 feet in the Blythswood drilled well, using a thermocouple of iron and copper. With this exception, practically all the early observations in deep wells were made with some form of maximum thermometer. The present maximum thermometer with a tight constriction above the bulb is a very satisfactory instrument for the purpose.

Fig. 1-F shows a set of three maximum thermometers mounted in a metal frame consisting of three wires, two thin plates, and six thin-walled copper tubes soldered together as shown in the figure. Cotton forced into the ends of the tubes holds the thermometers in place, and layers of cotton about ½ thick, placed above and below the frame, serve to hold it in a fixed position within the tubes C and D. Tubes C and D are attached to the end of the line only; but tube E, carrying the three thermometers F, and tube A carrying the three sealed tubes B, each of which carries a maximum thermometer, can be attached at any point on the line. Tubes A, B, C are used in water, D and E in air. The required exposure is about ¾ of an hour in water and 1¼ hours in air.

Tubes C, D, E are 13/16 inch I. D. The standard pipe plug in the upper end of tube C is ¾ inch diameter, No. 14 thread. It has withstood a pressure of 9000 feet of water without showing serious signs of leakage. Graphite paste is used to seal the plug in the tube.

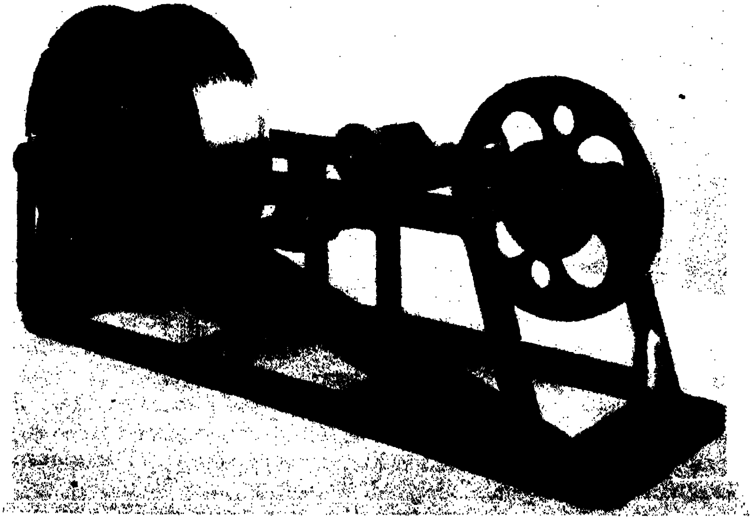


FIG. 2. Reel and measuring wheel for lowering maximum thermometers into deep wells. Total weight, including 12,000 feet of No. 17 stainless wire, 143 pounds.

The thermometers are graduated at intervals of 1° from the freezing point to the boiling point of water over a length of about 18 cm. Readings are easily estimated to tenths of a degree F with the assistance of a thermometer-reading telescope. The mercury is returned to the bulb by whirling the thermometers on the end of a string about 18 inches in length.

Fig. 2 shows the reel and measuring wheel used to lower the thermometers into the well. The distance from the center of the reel to the center of the measuring wheel is about 22 inches. The reel carries 12,000 feet of No. 17 stainless steel wire, diameter 0.045 inch, weight about 5.3 pounds per 1000 feet, total breaking load, 360 pounds. The measuring wheel is 7.5944 inches I. D. A set-back revolution counter records depths in feet. The spooling device in front of the reel is not only a great convenience; it is a necessity if accurate observations are desired. A brass packer or stuffing box for cleaning the line is shown on the front end of the machine, and a brass bob with slots cut into it like the ones shown at the lower ends of tubes C and D serves to connect these tubes to the end of the line. Sleeve *b* locks the tubes to the brass bob. A brake consisting of two steel bands is operated by a handle shown only in part in the figure. The speed of rotation of the reel with reference to the handle can be changed from a 1:1 to a 1:2 ratio by shifting the small bolt shown above the axle of the reel.

In operation, the machine is placed on a substantial box and, if necessary, anchored to the floor by means of a couple of ropes and 4 floor pins. Ordinarily, one man can operate the machine to depths of 1 mile or more. The rate of removing thermometers from the well is important and should not greatly exceed 100 feet per minute. They can be lowered at rates somewhat greater than 200 feet per minute. Two ice baths are used, one in which the tubes are placed immediately on removal from the well, and the other which serves as a receptacle for the thermometers until they are returned to the tubes for relowering into the well. The observations are made on the chilled thermometers so that the stem corrections can be interpolated from a table. It is easier and more accurate to make the observations in this way, for considerable time is required for the thermometer to acquire the temperature of the air when the well temperature is higher than the air temperature; and when the reverse is true, the readings must necessarily be taken on the chilled thermometers.

In 1924, Arctowski[1] developed a reel and measuring wheel for handling maximum thermometers in deep wells. The measuring wheel is attached to the top of a tripod and the reel is attached to one leg of the tripod. Kraskowski[2] likewise uses a tripod, but, in this case, the reel and measuring drum are mounted between steel plates which are attached to the top of the tripod.

Electrical Thermometers. In 1916, Johnston and Adams[3] observed the temperatures to a depth of 2500 feet in a deep well near Mannington, West Virginia, using an electrical resistance thermometer. The electric cable was ½ inch diameter; weight, about 0.088 pound per foot. It was carried on a temporary drum about 3 feet in diameter. Depths were measured on a wheel which recorded 8 feet of cable for each turn of the wheel. The resistance thermometer coil of nickel wire had a resistance of 250 ohms corresponding to a temperature coefficient of about 1 ohm per degree C. It was surrounded by a fusible alloy. The accuracy of the readings was somewhat less than 0.01 °C.

Immediately following the work of Johnston and Adams, the present writer[4] used a hand-operated electrical resistance thermometer outfit in testing 8 deep wells in West Virginia and 1 deep well at Bessie, Oklahoma. Some of the readings were taken at a depth of 3000 feet. The platinum thermometer was of the Leeds and Northrup quick-acting type with a resistance of 252.30 ohms at 0 °C, or a variation of about 1 ohm per °C. A time interval of about 20 minutes was required for the thermometer to reach equilibrium in air when readings were taken at intervals of 100 feet. The cable consisted of one No. 20 steel aviator wire and two No. 21 enameled copper wires; O. D. of cable about 3.3 mm, breaking load 200 pounds, total weight about 15 pounds per 1000 feet. Each of the three wires was inclosed in a double thickness of cloth insulation used by the U. S. Signal Service on buzzer wire. After being cabled, the three wires were inclosed in a stout braid and saturated in a moisture-repelling compound. The results were highly satisfactory, but the tests showed clearly that equipment of this kind would be very expensive on account of having to make frequent replacements of the cable.

The problem of making temperature surveys on a large scale, particularly in the oil fields, has been solved by Schlumberger[5] who adapted his electrical resistance equipment for electrical coring to the measurement of temperatures. The method has the advantage of obtaining a continuous record. Unfortunately, most of the wells tested are not in temperature equilibrium, so that true rock temperatures are not recorded; and as the tests are frequently made in very deep wells filled with heavy mud, the equipment is much heavier than is generally needed for temperature tests, at least, in most of the wells. Schlumberger's researches have made temperature surveys and electric surveys a permanent part of oil-field development and operation.[6]

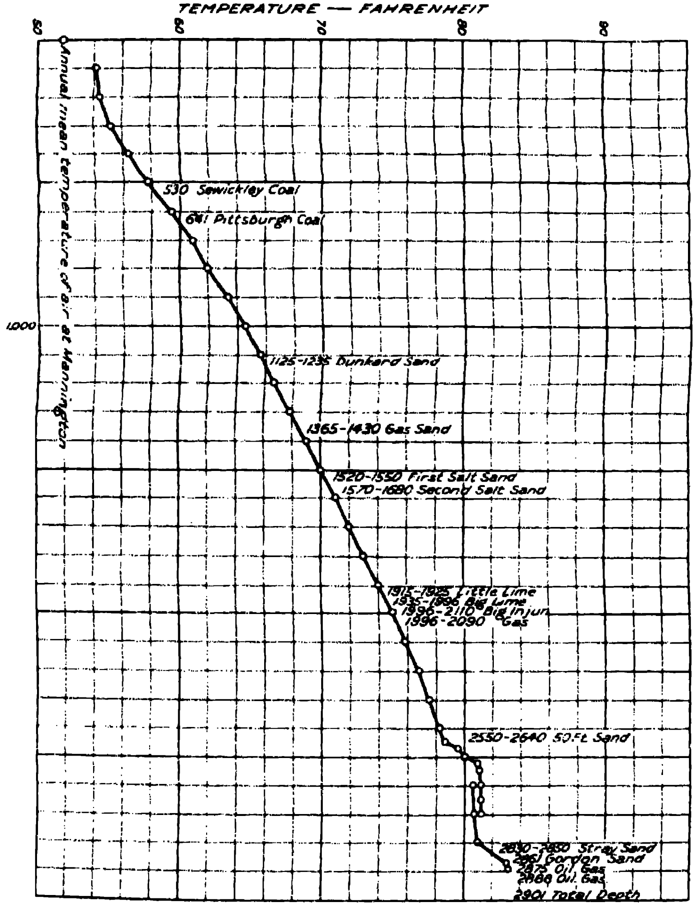


FIG. 3. Depth-temperature curve. C. D. Morgan No. 7, South Penn Oil Company, Mannington, West Virginia.

Recently, Weiss[7] has elaborated equipment of the Johnston-Adams type and obtained an accuracy of 0.01 °C to a depth of 4710 feet in a well about 18 miles southeast of Johannesburg. The 6000-foot cable was 0.802 inch in diameter and weighed nearly 3000 pounds. Depths were measured on a 10-foot wheel. Hand power was used, but the machine is easily adapted to machine power. From 20 to 25 minutes were required for the thermometer to reach thermal equilibrium when readings were taken in water at intervals varying from 70 to 100 feet in a 53-mm hole.

Comparison of Maximum Thermometer and Electrical Resistance Thermometer Methods

The electrical resistance thermometer is more accurate than the maximum thermometer and where detail is of importance, it is more convenient and more trustworthy. An illustration is provided in the depth-temperature curve of Fig. 3.[4a] The cooling effect of the gas from depths of 2875 and 2888 feet is shown at the bottom of the well, and again at the depths 2450-2525 feet where the gas was expanding as it escaped from the pool of oil. The lower curve from 2600 to 2888 feet was obtained after the level of the oil had been lowered a few feet by bailing. The curve shows that the increased flow of gas which resulted from lowering the level of the oil reduced slightly the temperature of the oil in the pool.

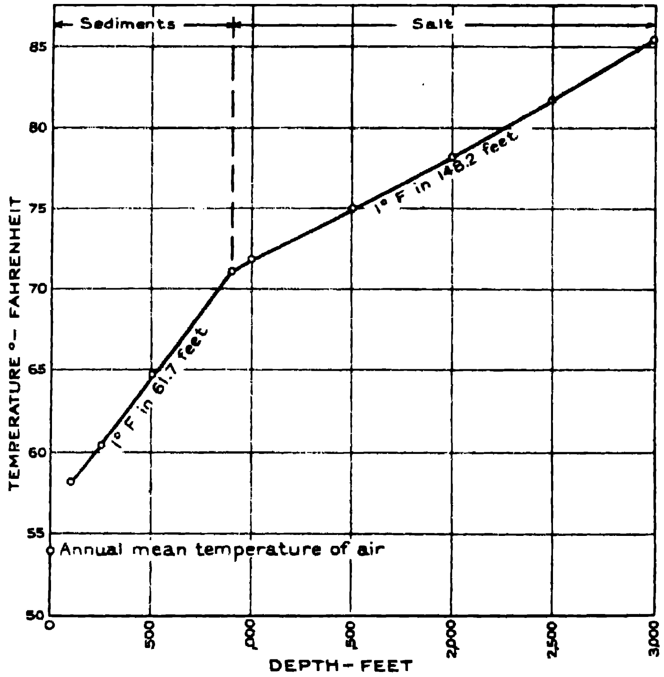


FIG. 4. Depth-temperature curve. Balsley No. 1, Utah Southern Oil Company, Grand County, Utah.

The records shown in the upper part of Fig. 3 are vitiated to a certain extent by small flows of gas from the bottom of the well. Even so, the curve shows that the rise in temperature at the points where the well cuts through the Sewickley and Pittsburgh coal beds is apparently imperceptible. However, refined measurements under ideal conditions might show the location of the beds.

Now that stainless steel wire can be obtained, the only replacements needed with the maximum thermometer method are new thermometers and occasionally a new measuring wheel. Replacement of the thermometers is not much of an item, for the loss by breakage is practically negligible and the loss by deterioration is not very large. With continued usage, a maximum thermometer ultimately records too low. The cable, of course, is the important factor in the electrical equipment.

It is to be hoped that improvements in construction will soon permit the use of a cable of greatly diminished weight so that the electrical method can be adopted for general use. A real advantage of the maximum thermometer outfit is its light weight (see Fig. 2). It can often be used in abandoned wells or wells isolated by floods that cannot be reached even with light-weight cars.

Reliability of Observations

Concerning questions of precision, it must be borne in mind that ideal laboratory conditions are not generally found in deep wells. Moisture in rocks and various combinations of oil, gas and water may cause rather wide departures from anticipated theoretical results. A good instance of this kind of failure is to be found in a comparison of the observed depth-temperature curves with the curves predicted on the basis of thermal conductivities of the strata. Fig. 4 shows a depth-temperature curve in dry sediments above a salt bed which approaches laboratory conditions very closely, but ordinarily the curves do not show a definite demarcation between strata. Notwithstanding these defects, the depth-temperature curves are frequently capable of an approach to rigorous interpretations as has been shown by Lang.[8] In Fig. 3, the differences in the trends of the depth temperature curve through the strata have been obliterated, probably by moisture and a small flow of gas.

Units of Measurement

The gradients and the reciprocal gradients, as well as the original observations, are expressed in both the British and the metric systems of units, and in some instances a combination of the two systems has been used. The relations between the units commonly employed are as follows:

1 °F per foot = 1 °C per 0.548641 meter
1 °C per meter = 1 °F per 1.822685 feet
1 °C per foot = 1 °F per 0.555556 foot
1 foot per °F = 0.548641 meter per °C
1 meter per °C = 1.822685 feet per °F
1 foot per °C = 0.304801 meter per °C
1 foot per °C = 0.555556 foot per °F

Graphical Representation of Temperature Data

Another question that arises is the method of plotting the observations. It seems that the xy-coördinate system should be retained where x, as usual, is the independent variable and y (or θ) is the dependent variable; or, in this case, the observed temperature at a given depth (x). Confusion arises, also, in regard to the sign of x. If plotted so as to represent actual conditions, x and y are interchanged, and x is a negative quantity which, of course, necessitates changing the signs of certain terms in the mathematical equations. A clockwise rotation of the axes shown in Fig. 4 through an angle of 90° is a possible solution of the problem. It is very desirable that some kind of standard practice as regards both units and methods of representation of the data of observation be adopted.

In the case of structure maps, a graph showing the geologic structure and the related geothermal surfaces by means of contours seems to be a satisfactory method of representing the data;[9] but, in those cases where the observations are limited to bottom-hole temperatures, it is necessary to use the less accurate method of plotting the reciprocal gradients as determined from a single observation at the bottom of the well and the annual mean surface temperature of the air at the station plus 1 °F, or more, depending on location, for excess of soil temperature over air temperature (Fig. 5). Strong[10] emphasizes the importance of sections in preferance to contours on the isogeothermal surfaces.

Thermal Constants

The data of observation represented graphically in Figs. 3 and 4 could be represented analytically by means of a truncated power series. Instead, however, it is generally sufficient to use the simple equation

$$\theta = a + bx \tag{1}$$

to represent the entire curve or certain segments of the curve.

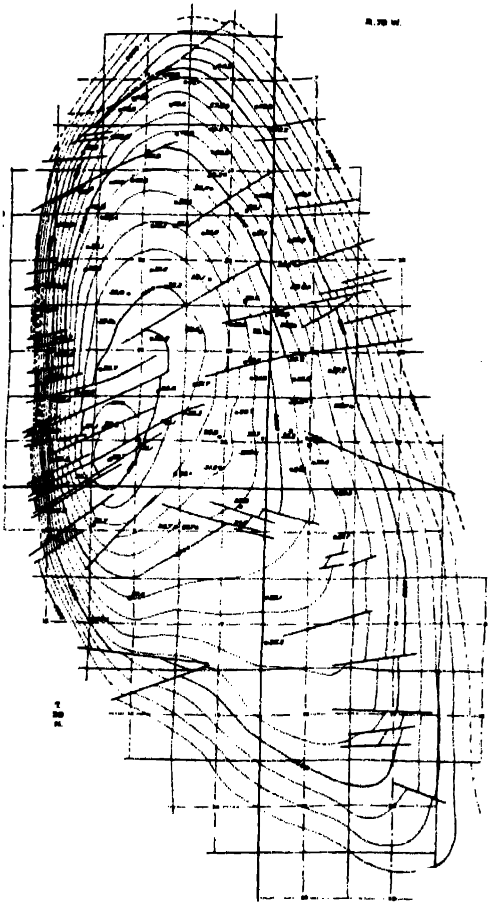


FIG. 5.

Salt creek dome showing distribution of reciprocal gradients (feet per °F). Contours are drawn on the second Wall Creek sand.

In Tables 1 and 2, the constants are given for the entire curve and from 2000 feet to the greatest depth at which an observation was made.

The constants a and b, adjusted by the method of least squares, and the related constants e, $1/b$, and r, may be considered as the thermal constants for that particular point on the surface of the earth. In most cases, comparison of the two values of $1/b$ indicate correctly the direction of curvature of the depth-temperature curve at that location.

Table 1. Temperature Gradients and Related Constants in the United States. British Units.

Town or field	*e*	100 feet to greatest depth				Greatest depth	2000 feet to greatest depth				Elevation
		a	*b*	1/*b*	*r*		*a*	*b*	1/*b*	*r*	
	°F	°F	°F/ft	Ft/°F	°F	Feet	°F	°F/ft	Ft/°F	°F	Feet
Alabama											
Vernon	+ 0.3	61.26	0.00952	105.0	0.36	3500	60.63	0.00978	102.2	0.16	324
California											
Alamitos Heights	− 9.5	71.83	0.02111	47.4	0.35	4500	72.61	0.02087	47.9	0.27	
Bakersfield	−12.4	70.73	.01569	63.7	2.36	4250	58.45	.01930	51.8	1.79	940
Coalinga	− 8.4	71.17	.01964	50.9	0.02	4320	70.53	.01982	50.5	0.19	
Fullerton	− 9.4	72.78	.01919	52.1	0.73	4270	73.34	.01906	52.5	0.76	
Grass Valley	− 0.3	54.67	.00525	190.4	0.27	3400	56.10	.00472	211.9	0.11	2200
Huntington Beach	− 6.5	66.54	0.02705	37.0	0.90	4000	62.26	0.02846	35.1	0.48	
Long Beach	− 8.9	67.28	.01985	50.4	0.95	9000	64.96	.02021	49.5	0.63	339
Santa Fe Springs	− 8 5	71.68	.01924	52.0	0.47	4525	74.24	.01849	54.1	0.16	155
Seal Beach	− 1.1	66.68	.02256	44.3	1.46	3500	67.59	.02204	45.4	0.12	10
Ventura	− 8.1	67.38	.01635	61.2	0.29	3500	67.60	.01630	61.3	0.07	57
Whittier	−12.2	73.10	0.01874	53.4	0.63	3750	74.82	0.01825	54.8	0.38	450
Colorado											
Calhan	− 5.9	50.10	0.01712	58.4	1.06	4000	43.40	0.01924	52.0	0.66	
Florence	− 2.5	54.28	.02151	46.5	1.02	3500	47.23	.02398	41.7	0.90	
Fort Collins	− 6.2	50.41	.01956	51.1	0.98	4000	44.42	.02146	46.6	0.54	
Longmont	− 8.4	50.74	.02399	41.7	2.18	6500	44.16	.02546	39.3	0.85	
Kansas											
Syracuse	− 2.5	55.00	0.01428	70.0	1.29	4600	46.72	0.01655	60.4	0.58	3460
Louisiana											
Haynesville	+ 0.2	64.41	0.02245	44.5	0.80	2750	70.36	0.02011	49.7	0.00	
Pine Island	+ 0.4	69.13	.02218	45.1	1.44	3500	76.26	.01956	51.1	0.47	
Zwolle	− 4.8	69.03	.02191	45.7	0.75	3380	72.54	.02063	48.5	0.78	312
Michigan											
Houghton, Baltic 16	......	......	......	......	......	6250*	36.29	0.00922	108.4	0.10	
Keweenaw Point	− 3.1	43.44	0.00852	117.4	1.31	5367	41.83	.00883	113.3	1.28	
Surrey Tp., Clare Co.	0.0	40.14	.01887	53.0	2.20	3700	27.34	.02338	42.8	1.01	
Montana											
Kevin-Sunburst	− 4.4	47.16	0.00965	103.7	0.95	4090	45.11	0.01022	97.9	1.34	3548
New Mexico											
Artesia	− 5.1	68.86	0.00439	227.7	0.22	2892	69.78	0.00399	250.9	0.10	3060
Carlsbad	− 3.9	63.37	.00759	131.8	1.12	6000	59.52	.00844	118.5	0.77	3309
Lovington	− 1.7	68.01	.00554	180.5	1.86	4500	75.63	.00331	301.7	0.32	4400
Roswell	− 6.0	65.50	.00583	171.5	0.23	3000	64.35	.00630	158.7	0.25	3720
New York											
Steuben County	− 1.8	45.39	0.01608	62.2	1.02	4250	39.72	0.01778	56.3	0.29	1792
Allegany County	− 2.1	41.32	.01697	58.9	1.96	4700	31.84	.01952	51.2	1.22	2092
North Dakota											
Lonetree	− 6.1	40.00	0.01998	50.0	2.07	3750	27.86	0.02399	41.7	1.13	1969
Oklahoma											
Ardmore	− 0.9	62.53	0.00978	102.3	1.01	3000	55.22	0.01270	78.7	1.49	
Ardmore-Healdton	0.0	62.91	.00914	109.4	0.24	2750	62.61	.00928	107.8	0.12	
Billings	− 1.5	60.15	.01911	52.3	0.47	3500	60.06	.01916	52.2	0.43	
Burbank	0.0	57.34	.02188	45.7	0.97	2850	51.81	.02426	41.2	0.78	
Cromwell	+ 1.2	58.32	.02203	45.4	0.64	3000	52.54	.02436	41.1	0.33	
Davenport	+ 0.3	58.67	0.01162	86.0	1.01	3375	51.45	0.01425	70.2	0.42	
Dilworth	− 0.4	58.47	.01988	50.3	0.30	3375	57.79	.02013	49.7	0.07	1114
Holdenville	− 1.7	61.38	.02002	49.9	1.25	5200	57.21	.02101	47.6	0.62	
Hubbard	− 1.2	60.29	.02103	47.6	0.48	2870	55.02	.02314	43.2	0.42	
Newkirk	− 0.5	59.52	.02224	45.0	0.90	3000	53.37	.02460	40.7	1.54	
Okemah	+ 0.8	60.58	0.02313	43.2	0.51	2750	58.46	0.02388	41.9	0.64	
Oklahoma City	− 0.6	57.08	.01129	88.6	1.22	6000	52.95	.01224	81.7	1.11	
Oklahoma City	+ 2.4	54.67	.01161	86.2	1.14	6000	51.38	.01235	80.9	0.98	
Papoose	+ 0.4	59.16	.02182	45.8	0.82	3000	52.77	.02440	41.0	0.78	
Perry	+ 1.2	58.96	.01717	58.2	0.42	3000	56.08	.01830	54.6	0.00	

*From 4815 to 6250 feet

Table 1. Temperature Gradients and Related Constants in the United States. British Units—(*Continued*)

Town or field	*e*	100 feet to greatest depth				Greatest depth	2000 feet to greatest depth				Elevation
		a	*b*	1/*b*	*r*		*a*	*b*	1/*b*	*r*	
	°F	°F	°F/ft	Ft/°F	°F	Feet	°F	°F/ft	Ft/°F	°F	Feet
Oklahoma—(Cont.)											
Sasakwa	− 1.0	60.08	0.01878	53.3	0.63	3500	56.64	0.02004	49.9	0.20	
Seminole	− 1.0	57.30	.01679	59.5	2.16	4000	45.74	.02054	48.7	0.94	
Tonkawa	− 1.2	59.31	.02017	49.6	0.99	4000	53.34	.02204	45.4	0.92	
Wewoka	+ 0.7	59.86	.02100	47.6	0.37	3000	56.72	.02228	44.9	0.26	828
Oregon											
Astoria	− 0.9	51.07	0.01670	59.9	0.36	3780	50.41	0.01695	59.0	0.12	
Pennsylvania											
Gaines Jct.	− 1.8	41.04	0.01619	61.8	2.20	5500	31.49	0.01853	54.0	0.64	
Genesee Tp., Potter C.	− 0.9	41.16	.01638	61.1	1.85	5000	32.17	.01872	53.4	1.09	2106
Hebron Tp., Potter C.	+ 2.4	38.92	.01700	58.8	1.34	5250	33.33	.01836	54.5	1.01	2156
Johnstown	− 0.7	42.70	.01313	76.2	2.22	6500	37.54	.01421	70.4	2.19	2721
Long Bridge	+ 1.9	46.88	.01565	63.9	1.43	6815	43.33	.01632	61.3	1.31	1128
New Castle	+ 1.1	44.69	0.01621	61.7	1.94	4500	34.25	0.01924	52.0	0.45	
Texas											
Big Lake	− 0.2	66.37	0.00699	143.1	0.97	3175	26.18*	0.01713*	58.4*	1.73*	2884
Blue Ridge	− 1.7	69.97	.01800	55.6	0.54	2900	65.62	.01983	50.4	0.08	
Boggy Creek	− 1.7	64.85	.02867	34.9	2.27	3703	57.01	.03118	32.1	2.15	
Callisburg	− 0.6	64.14	.00982	101.8	0.42	3680	61.79	.01061	94.3	0.17	
Canadian	− 2.3	60.58	.01001	99.9	1.17	4758	55.57	.01142	87.6	1.01	
Damon	− 4.8	71.64	0.01619	61.8	1.03	4000	65.98	0.01800	55.6	0.45	
Del Rio	− 4.3	74.11	.01311	76.3	0.75	3686	79.98	.01119	89.4	0.20	
Eastland	− 3.8	65.93	.01885	53.0	0.46	3000	66.08	.01890	52.9	0.33	
Edwards	− 1.9	65.02	.01666	60.0	3.14	6600	45.40	.02037	49.1	0.86	1770
Graford	− 3.3	67.32	.01856	53.9	0.76	3000	62.68	.02050	48.8	0.33	1083
Graham	− 2.1	66.36	0.01732	57.7	0.90	4334	61.46	0.01869	53.5	0.95	
Guthrie	− 3.1	66.40	.00898	111.3	1.07	2950	56.05	.01291	77.5	1.53	
Long Point	− 2.2	71.68	.01765	56.7	0.46	3300	73.78	.01682	59.5	0.16	
Mexia	− 0.7	66.16	.02296	43.6	0.36	3000	67.67	.02240	44.6	0.07	
Ozona	− 0.9	60.18	.01624	61.6	2.03	5500	53.64	.01786	56.0	1.14	
Pampa	− 2.0	61.59	0.00847	118.0	0.73	5000	61.27	0.00854	117.1	0.94	2705
Panhandle	− 3.1	61.05	.00674	148.3	0.32	3425	59.03	.00744	134.4	0.30	3240
Panhandle	− 2.0	61.33	.00833	120.1	0.66	4190	58.68	.00913	109.5	0.64	
Pierce Jct.	− 3.5	72.50	.01753	57.0	0.36	3300	74.72	.01668	59.9	0.10	58
Ranger	− 3.0	65.44	.02113	47.3	0.60	3000	59.42	.02350	42.6	0.50	
Utah											
Grand County	− 5.1	57.29	0.01009	99.2	1.02	4800	53.87	0.01100	90.9	0.63	
Washington											
Moclips	+ 3.1	44.37	0.01378	72.6	0.79	3500	40.67	0.01524	65.6	0.10	163
West Virginia											
Bridgeport	− 2.3	49.75	0.01401	71.4	2.97	7310	40.78	0.01572	63.6	2.10	1161
Fairmont	− 1.5	49.24	.01521	65.8	2.43	7500	40.06	.01698	58.9	2.23	1201
Grantsville	0.0	52.71	.01204	83.1	0.76	4500	47.03	.01391	71.9	0.47	
Spencer	+ 0.7	53.12	.01179	84.8	0.22	3250	51.54	.01240	80.6	0.15	875
Volcano	− 0.7	49.02	.01476	67.8	1.98	4400	39.09	.01768	56.6	0.59	1216
West Union	+ 0.5	45.73	0.01385	72.2	2.73	6500	36.44	0.01579	63.3	1.47	1138
Wyoming											
Big Muddy	− 3.4	49.87	0.01884	53.1	0.52	3250	46.79	0.01999	50.0	0.37	
Cody	− 8.4	51.51	.01698	58.9	0.74	4250	55.39	.01587	63.0	0.52	5409
Lance Creek	− 6.5	49.43	.02720	36.8	0.53	3500	50.35	.02690	37.2	0.15	
Lost Soldier	− 2.3	48.87	.02569	38.9	2.06	3400	56.06	.02282	43.8	0.47	
Rawlins	− 2.0	42.76	.01751	57.1	1.15	3000	33.17	.02140	46.7	0.44	6950
Rock River	− 3.7	46.30	0.01431	69.9	0.41	3000	39.99	0.01690	59.2	0.44	
Salt Creek	− 3.7	47.83	.02079	48.1	1.03	2650	41.13	.02398	41.7	0.71	4955
Teapot	− 2.8	46.46	.02744	36.4	1.16	2736	42.92	.02920	34.2	0.58	
Little Sand Draw	− 4.8	47.26	.01612	62.0	0.58	3000	42.48	.01812	55.2	0.34	4792

*5475–8300 feet

Table 2. Temperature Gradients and Related Constants in Foreign Countries. British Units.

Towns or section of country	e	Range of depths		a	b	$1/b$	r	Approximately 2000 feet to greatest depth			
								a	b	$1/b$	r
	°F	Feet		°F	°F/ft	Ft/°F	°F	°F	°F/ft	Ft/°F	°F
Cape of Good Hope											
Carnarvon	− 9.7	100	5003	79.69	0.01694	59.0	3.21	94.89	0.01273	78.5	0.49
Transvaal											
Witwatersrand	+ 1.2	495	3916	61.57	0.00517	193.6	2.47	54.84	0.00736	135.8	1.06
Witwatersrand	− 1.7	1000	2925	64.97	.00448	223.4	0.55	68.30	.00318	314.7	0.58
Witwatersrand	− 2.6	100	4710	64.38	.00591	169.1	0.84	58.22	.00754	132.6	1.61
Australia											
Great Basin	− 1.7	720	3000	76.13	0.01551	64.5	4.39	62.17	0.02121	47.1	2.69
South	+ 8.9	1360	4700	86.42	.02750	36.4	5.41	108.73	.02164	46.2	4.33
Austria-Hungary											
Pribram	− 2.9	244	2917	48.17	0.00817	122.4	0.49	51.34	0.00690	144.9	0.38
France											
Rouchamps	− 2.0	984	3310	47.95	0.02076	48.2	0.66	42.47	0.02262	44.2	0.44
Germany											
Paruschowitz	− 8.3	121	6427	50.88	0.01600	62.5	1.14	48.39	0.01654	60.4	1.08
Schladebach	− 2.8	118	5630	49.16	.01537	65.1	0.74	46.93	.01591	62.9	0.72
Sennewitz	+ 1.3	1480	3556	48.95	.01168	85.6	0.78	48.62	.01177	85.0	0.72
Sperenberg	−11.3	721	4162	62.13	.01449	69.0	1.52	68.57	.01258	79.5	2.05
Netherlands											
Oploo	− 4.8	650	3281	53.18	0.01648	60.7	0.52	49.49	0.01775	56.3	0.26
Sevenum	− 6.0	328	3281	55.51	.01618	61.8	1.52	44.25	.02025	49.4	1.77
Witwaterings	+ 4.8	984	4085	43.55	.01884	53.1	0.97	41.95	.01933	51.7	1.21
Woensdrecht	− 6.1	755	3937	48.30	.02088	47.9	2.04	41.12	.02324	43.0	2.80
Poland											
Bitkow	+ 0.2	164	3117	44.13	0.01126	88.8	0.58	40.08	0.01286	77.7	0.63
Boryslaw	− 2.1	164	4921	45.33	.01463	68.3	0.73	45.60	.01459	68.5	0.63
Boryslaw	− 1.9	164	4183	44.81	.01474	67.8	0.85	42.97	.01535	65.1	0.69
Boryslaw	− 2.7	328	4429	46.47	.01178	84.9	0.86	41.53	.01318	75.9	0.71
Boryslaw	+ 0.2	164	5413	39.15	.01351	74.0	1.88	31.49	.01544	64.8	1.23
Tustanowice	− 4.9	164	3937	45.91	0.01412	70.8	1.34	37.69	0.01683	59.4	0.30
Russia											
Bibi-Eibat	− 9.3	875	3234	66.93	0.01739	57.5	3.48	72.30	0.01510	66.2	2.68
Donetz Basin	− 5.5	312	3937	49.90	.01586	63.1	1.10	47.41	.01683	59.4	0.89
Canada											
Ontario	− 0.5	248	3065	36.82	0.00610	164.0	1.04	39.36	0.00494	202.5	0.25
Ontario	− 7.5	235	3892	40.91	.00448	223.4	0.19	41.09	.00441	226.6	0.22
Ontario	− 7.5	181	3865	41.51	.00429	233.2	0.33	40.85	.00448	223.1	0.12
Ontario	− 3.8	1100	4225	38.18	.00725	137.9	0.17	38.52	.00715	139.9	0.18
Ontario	− 7.8	391	3575	41.51	.00599	167.1	0.18	41.27	.00608	164.4	0.19
Ontario	− 4.0	587	3003	36.27	0.00845	118.4	0.90	41.43	0.00590	169.4	0.29
Ontario	− 4.3	495	2993	38.30	.00703	142.2	0.24	38.82	.00684	146.3	0.44
Ontario	− 6.7	400	3100	45.84	.00644	155.2	0.68	48.74	.00542	184.6	0.88
Colombia											
Puerto Wilches	+ 2.2	100	3100	78.73	0.00840	119.0	0.79	78.31	0.00877	114.0	0.49
Mexico											
Tuxpam	− 5.6	75	4080	75.97	0.02481	40.3	3.45	65.71	0.02810	35.6	3.04

The quantity r is the computed probable error of an observation of weight unity. As the instrumental error of an observation at any depth does not ordinarily exceed 0.3 °F, it follows that a large value of r implies that the depth-temperature curve possesses a marked curvature. Examples of this kind of curve are to be found in the data of Pennsylvania and West Virginia. Exceptions to this rule are to be found at Keweenaw Point, Michigan, where the constants were evaluated from 70 observed points not in the same vertical, and at Bibi-Eibat, Russia, where the calculated values are based on 139 observed points distributed throughout the field. The calculated values at Grass Valley, California, are based on 20 observations in a mine which are located approximately on a vertical line.

The value of e, the excess of soil temperature over air temperature, is calculated from the annual mean temperature of the air given in the columns of Climatological Data of the U. S. Weather Bureau and the value of a computed from a least square adjustment of the observations, preferably from 100 to 1000 feet. As the Weather Bureau stations are frequently at a considerable distance from the well, allowance must be made for the possibility of errors in the interpolated values of the mean annual temperatures of the air. In foreign countries, some of the values of e have been computed from approximately the first 1000 feet below the minimum depth, which in several instances is a few hundred feet beneath the surface of the ground. Additional errors are thus introduced into the calculations.

The first set of constants is to be used in interpolating the temperatures from 100 feet to the greatest depth in the well. For extension of the curves to greater depths, the second set of constants is generally to be preferred for the effects of surface topography and excess moisture in the surface rocks are largely eliminated by this procedure.

Interpretation of Variation in the Thermal Constants of Tables 1 and 2

A detailed analysis of the tabulations contained in Tables 1 and 2 cannot be undertaken here. It must suffice for the present to call attention to a few conclusions that are more or less obvious.

First, with regard to values of e, it will be noted that large values are found in the semi-arid regions of California and New Mexico and in the snow-covered areas of Ontario, Canada, and possibly of Colorado. In areas of more rain-fall, however, the values vary from almost nothing to 2° or 3 °F. Calendar [11] has shown that rains and melted snow lower the isogeotherms of the soil; snow causes them to rise.

The loss of heat from the surface of the earth by radiation is equal to $e \times$ constant of emissivity, and is therefore proportional to e.

It will be noted that the temperatures in many of the oil and gas fields are high, as for example the temperatures in the gas field of southern Michigan in comparison with those in the copper-bearing area in the northern part of the state; or, again, the temperatures in the oil fields of southern California are high in comparison with those in the gold mine at Grass Valley. In southeastern New Mexico, the Panhandle of Texas, and in the western part of Oklahoma, low temperatures prevail in old rocks of Permian age.[12] The causes of the low temperatures in this large area are probably lapse of time and the undisturbed state of the rocks. In the mining areas of Grass Valley, Houghton, Keweenaw Point, Ontario, and Witwatersrand, the low temperatures are probably the result of intrusives and ascending hot waters that brought enormous quantities of heat to the surface of the earth by the process of convection. The first effect of the intrusives and ascending hot waters is to heat the surface rocks; but, in the course of millions of years after the intrusives and hot waters have ceased to rise, the temperatures in the area will be greatly reduced because of the transfer of heat in the past by both convection and conduction.

In many sedimentary areas represented chiefly by oil fields, the reciprocal gradients do not vary greatly from 50 feet per °F. The values of the reciprocal gradients in the synclines surrounding the oil fields are practically unknown, but a few observations indicate that they are probably large. The fact that the temperatures in the sediments are generally high in comparison with those in an undisturbed, cooling earth is the result in part of the blanketing effect of the sediments. Calculations by Dr. Jeffreys[13] show that the temperatures at the bottom of a sedimentary column that has sunk about 10 kilometers below sea level in 130 million years will rise to the extent of about 250 °C. This being true, it is to be expected that during the subsequent period of uplift and erosion, the temperatures in the sedimentary blankets and the uplifted basement rocks would continue to be too high throughout long periods of time. Jeffreys shows also that the heat of adiabatic compression at the bottom of the sedimentary column is about 1 °C.

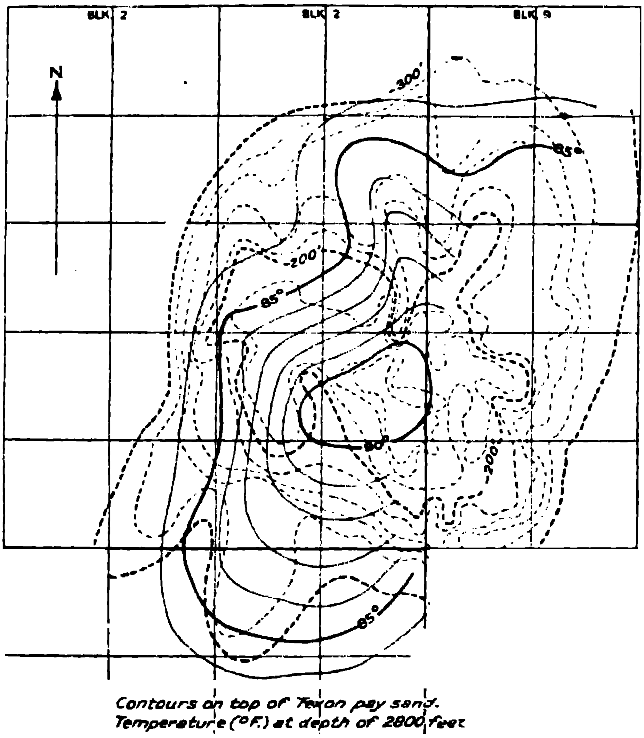

BLK 2
BLK 2
BLK 9
N
300
200
85°
85°
80°
200
85°
Contours on top of Texon pay sand.
Temperature (°F) at depth of 2800 feet

FIG. 6. Temperatures in the Big Lake field, Reagan County, Texas.

Relation of Temperature to Geologic Structure

Coincident geothermal and geological anticlines have been found at a sufficient number of points on the surface of the earth to suggest a universal relationship, at least under certain limitations.

At Boryslaw field, Galicia, H. Arctowski[14] established a well-defined relationship between geothermal and geological anticlines. M. W. Strong[15] shows a very interesting section across parts of Masjid-i-Sulaiman and Haft Kel fields, S. W. Iran. The isogeotherms rise over both anticlines and drop in the syncline between them. The upper isogeotherms over Masjid-i-Sulaiman are depressed on account of seepages of oil and gas. Another section in S. W. Iran shows depressed isogeotherms over a limestone fold buried beneath salt, anhydrite and marl. This exception to the general rule is explained by Strong on the basis of differences of thermal conductivities, limestone being a poor conductor in comparison with salt, anhydrite and marl. The reciprocal gradients vary from 5 to 13 °F per 1000 feet on the Masjid-i-Sulaiman structure, and from 9 to 19 °F per 1000 feet over the Haft Kel field.

Fig. 5 shows the distribution of about 100 reciprocal gradients over the Salt Creek dome [16] which are based on bottom-hole temperature measurements by the Stanolind Oil and Gas Company. The increase in the values of the reciprocal gradients from the crest to the flanks of the structure is slightly irregular, as may be expected when the variations in depths of the wells, the curvature of the depth-temperature curves, and the somewhat disturbed thermal condition of the wells are taken into account. The records as a whole, however, confirm and extend the evidence based on my observations of 1922 and 1923.[9]

The Salt Creek dome was formed during the late Cretaceous and Eocene period of orogenic activity and was soon after truncated to the extent of about 2 miles.[17] The rapid changes of temperature over the structure may be the result, therefore, of unequal uplift such that the isogeotherms have not had time to readjust themselves; or perhaps the dome was formed by a plug that now stands at a depth of about one mile beneath the surface of the ground over the top of the structure. Another possibility is proximity to hot rocks; and to this we add a fourth, namely, differences in thermal conductivity along and across the bedding of the strata.

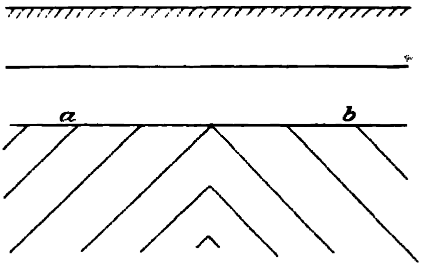


FIG. 7.

Sketch showing arrangement of strata in an angular unconformity.

As a means of generalizing to a certain extent the evidence of the Salt Creek field, a comparison of the magnitude and distribution of gradients in this field with the same at Big Lake, Texas,[18] (Fig. 6) is of importance.

Fig. 5 shows that the reciprocal gradients at Salt Creek vary from 29.6 feet per °F on the top of the structure to more than 60 feet per °F in the surrounding syncline. At Big Lake, Hawtof [18] gives 111.2 feet per °F on top of the structure and 148.2 feet per °F in the syncline about 14 miles northeast of the Big Lake field.

The great difference in the numerical magnitude of the reciprocal gradients, 29.6 and 111.2 feet per °F over the crests of the respective structures suggests that the Big Lake field has been static through a long interval of time. This conclusion is in agreement with information given me by Dr. Philip B. King of the U. S. Geological Survey. He says, "Evidence thus indicates that the Big Lake dome is entirely pre-Cretaceous, that much of the doming took place in later Permian time, and that earlier doming had taken place before the Permian." Recent uplift, therefore, is not the cause of the wide range in the values of the reciprocal gradients, nor is the magnitude of the closure, for it is only about 125 feet in this field. At Salt Creek, the closure on the oil-bearing portion of the Second Wall Creek sand is 1400 feet.

As the sequence of events at Big Lake fails to explain the wide range in temperature which exists in that field, it appears that differences in thermal conductivity may offer a possible solution of the problem.

In the first place, evidence indicates increased folding at considerable depth. That is, we may have an arrangement of the strata known as an angular unconformity, which is represented roughly in Fig. 7. If the rocks conduct more heat along the strata than across them, there will obviously be an excess of heat along *ab*; and if the horizontal strata above *ab* possess a thermal conductivity equal to or less than that of the inclined strata, the gradient through the horizontal strata will be greatly increased. The question as to the possible magnitude of this difference has been answered by Edward Hull,[19] who states that the temperature

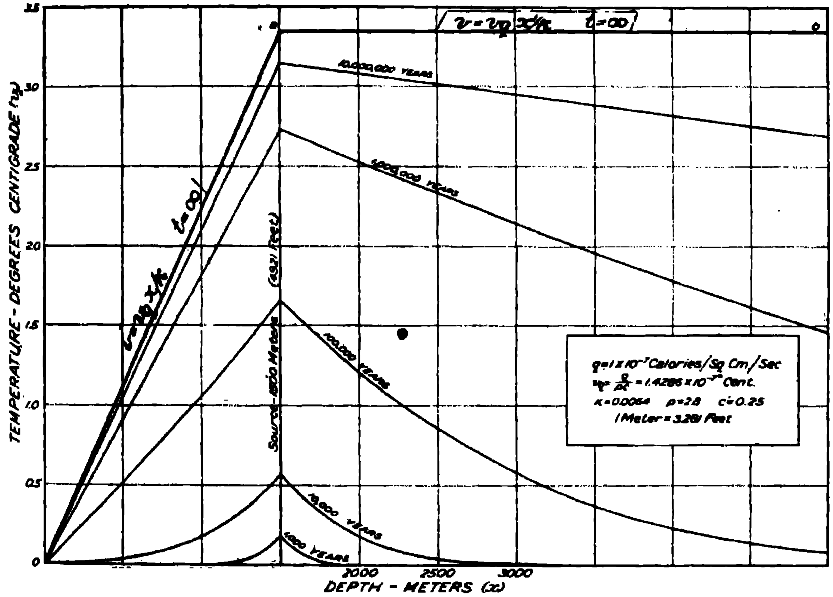


FIG. 8. Rise in temperature due to a heat source at a depth of 1500 meters.

in the highly inclined strata, 30° to 60°, at Dunkinfield Colliery, Cheshire, increases at the rate of 1°F in 77 feet, whereas the rate at Rose Bridge Colliery, Wigan, in horizontal strata of the same physical properties is 1°F in 54.4 feet. Results of a somewhat similar character have been reported by David T. Jones.[20]

The preceding results indicate rather strongly that recent uplift is not the only cause of variations in temperature over domes and anticlines.

Generation of Heat in Oil Beds

In the usual treatment of this subject it is generally assumed that the generation of heat in a bed would be manifested by a rather abrupt rise of the temperatures within the bed. Reference to Fig. 8, which is based on rigorous mathematical theory,[21] shows that this hypothesis is correct for time intervals of the order of magnitude of tens of thousands of years; but, for greater time intervals such as represent the age of an oil or other mineral deposit, the depth-temperature curve approaches two straight lines, *oa* and *ab* (Fig. 8) which intersect within the bed. The addition of the ordinates of these two approximately straight lines to the undisturbed depth-temperature curve (*a*, *d*) (Fig. 9) results in a curve like *abc* (Fig. 9) with a concavity toward the depth axis at the heat source. This conclusion is based on the assumption that the thermal conductivities of the rocks above and below the heat source are identical. Curves like *abc* (Fig. 9) have been found at El Dorado, Kansas; Coalinga, California; Big Lake, Texas; and in other fields. In fact, about 35 per cent of the curves are of this form; 5 per cent are straight lines; and the remaining 60 per cent are convex toward the depth axis. It cannot be assumed however, without a more detailed investigation, that the concave curves are the result of a generation of heat.

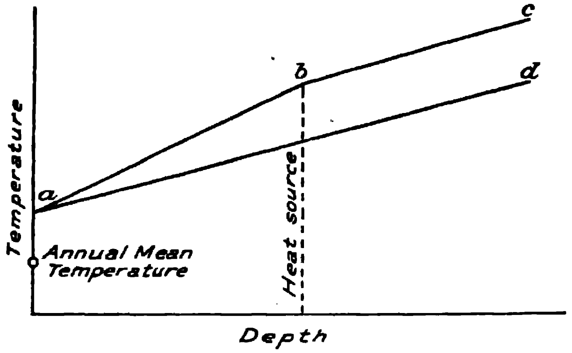


Fig. 9.

Sketch showing depth-temperature curve, *abc*, when heat is being generated in a single bed.

Important preliminary information in regard to the generation of heat in oil beds can be obtained from a study of the depth-temperature curve of Nesa 11 (Fig. 10). Dr. Parker D. Trask of the Geological Survey advises me that the well passes through a more or less continuous series of oil beds between the depths of approximately 3200 and 7300 feet. This curve, like about 40 other curves in this field, shows a slight rise at a depth of about 1000 feet. Dr. Trask believes that this slight change in the curvature is due to differences in the compaction of the rocks. At the bottom of the well, from 7000 to 9000 feet, the curve trends slightly downward, such that at 9000 feet the temperature is 1 or 2 °F too low. As Dr. Trask knows of no certain cause for the change in trend, it seems worth while to test the hypothesis of a generation of heat in the oil beds. On account of the great thickness of the beds, it will be necessary as a first approximation to assume that the total effect of the heat-generating sources is represented by the sum of a series of curves like *oab* (Fig. 8). Assuming constant thermal conductivities and a constant rate of generation of heat in each of the beds, it follows that the slope of the line *oa* (Fig. 8) will be the same for each assumed source of heat, and the sum of such curves (*oab*), displaced successively at equal intervals to the right, will result in a greatly magnified curve of the same form as *oab*. Hence the effect of a series of heat-generating beds is a greatly increased concavity at the level of the lowest heat-generating source and a marked convexity at the level of the highest heat-generating source. The depth-temperature curve of Nesa 11 can possibly be interpreted as fulfilling these requirements at approximately 3000 and 7000 feet, but the changes in the trends of the curve at these points are so slight that the evidence is not conclusive.

Another method of detecting the presence of oxidation in an oil bed is suggested by McCutchin's[22] observations over a sand lens at Haverhill, Kansas. The observations show that the temperatures in two producing wells on the sand lens are about 2.97 °F (1.65 °C) higher at a depth of 2500 feet (762 meters) than in an adjacent well at the same depth located beyond the edge of the producing area. As Haverhill is a structureless field, the temperature difference must be due to either the generation of heat within the bed, to difference in the thermal conductivity of the oil bed and the adjacent water-bearing sand, or possibly to a combination of these two effects.

Referring to Fig. 8, the rise in temperature at a depth of 762 meters due to a heat source, $q=1\times10^{-7}$ calorie/sq cm/sec=3.16 calories/sq cm/year is about 1.7 °C, which is a sufficiently close approximation to an assumed difference of 1.65 °C. Let it be assumed now that the heat-generating disk is 100 feet thick and that the pores occupy $\frac{1}{3}$ of the volume of the sand. Then a column of rock one square centimeter in cross-section and 100 feet in thickness contains about 900 grams of oil; and assuming the heat of combustion of oil to be 11,094 calories per gram, we have $(11{,}094\times900)/3.16=3.2\times10^{6}$ years as the time required to oxidize the entire bed of oil. As this result is inconsistent with geological facts, it appears that oxidation in the oil bed, if it occurs at all, is a rather insignificant source of heat.

Recent observations by Vladimirov, Kraskovski, and Semenov[23] show that the observed depth-temperature curve passing through a sulfide vein in Monchre-Tundra is a straight line. Here again, proceeding on the basis of equality of conductivities, the observations show that the sulfide vein is not a source of heat.

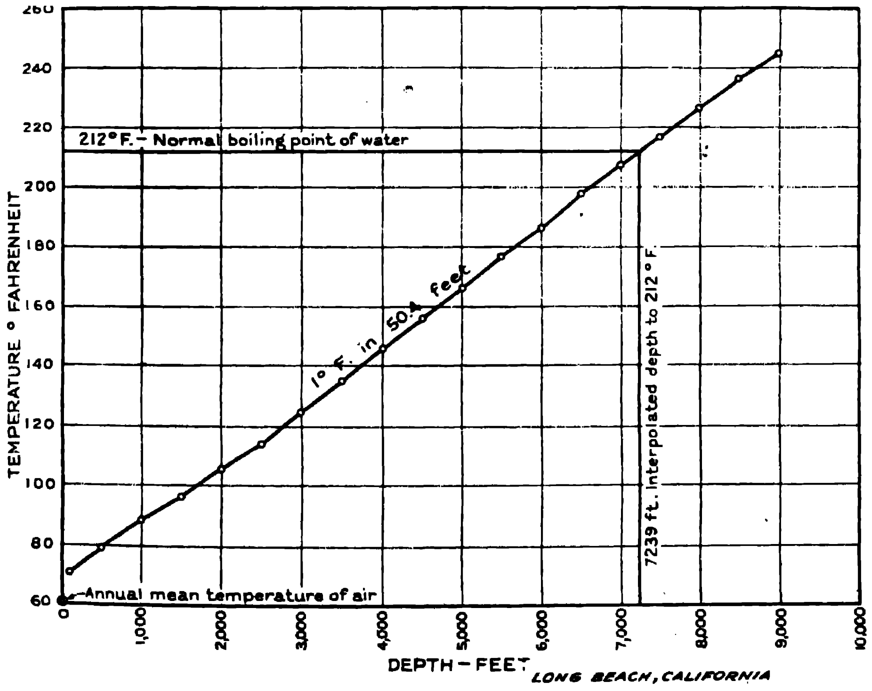


FIG. 10. Depth-temperature curve, Nesa 11, Shell Oil Company, Long Beach, California.

Heat of Radioactivity

On the editorial page of a recent issue of *The Telescope*, a publication of the Harvard Astronomical Observatory,[24] we find this statement with reference to a picture of a lunar landscape.

"The reproduction shows clearly an important but seldom mentioned formation that appears below and to the left of Copernicus. This consists of a long winding chain of more than three dozen craterlets. Strung along in so perfect a geometric pattern, this array of craters offers testimony for the correctness of the hypothesis of volcanic origin and against the hypothesis of meteoric origin. Such an arrangement could scarcely have come about as the result of a chance impact of meteors. Yet it might well have been produced by the presence of a long fault, with a weak region of the crust forming the physical basis for the adjustment."

This important conclusion of the Harvard astronomers eliminates the hypothesis of an initial cold-earth as well as the other hypothesis of an earth in which all the heat is due to radioactivity. The craters of the moon were once molten rock. Just what the temperatures were we do not know, but the surface of the moon must at one time have been a sea of molten rock.

By analogy, the surface of the earth must have passed through the molten state and in the subsequent process of refrigeration its surface may have closely resembled the lunar surface with its depressed areas—sea floors as they are called—and its elevated areas which correspond to the original continental masses. The original depressed areas are still in the main the ocean floors, and the elevated areas have continued to be the continental masses. These primitive areas of elevation and depression were the direct result of the cooling process during which the earth and the moon passed from the liquid to the solid state.

It is interesting to note that lines of volcanoes which apparently follow a fissure probably much the same as on the moon are found in Iceland and Nicaragua.[25] Following solidification, the surface of the earth has been subjected to the processes of erosion, uplift, and subsidence which have greatly influenced the temperatures of the rocks; for, independently of heat losses by conduction, there have been great losses of heat by convection resulting from uplift in local and regional areas, and, in areas of mineralization, by the movement of intrusives and ascending hot waters. Metamorphism is another factor that has greatly modified the temperatures of the rocks.

Ver Wiebe[26] divides the oil-producing areas of the United States into 11 provinces which are supposed to be the result of tectonic influences. It may be possible in the course of time to show the relation of the gradients in each province to its physical features; but for the present we shall merely call attention to the possible dependence of the temperatures on radioactive heat.

According to Joly,[27] the rate of generation of heat in sediments is 1.66×10^{-13}; in granite, it is 3.0×10^{-13}; this leaves an excess in the granite of 1.34×10^{-13} calorie/second/gram. Jeffrey's recent determination as quoted by Gutenberg[28] is 0.86×10^{-13} for sediments and 1.11×10^{-13} for granites of North America, Greenland, Iceland, Scotland, Ireland, and Japan, leaving a difference of 0.25×10^{-13} calorie/second/gram, or a reduction of 81 per cent from Joly's value.

Joly's difference of 1.34×10^{-13} calorie/gram/second amounts to 0.3609 calorie/1000 feet/year. The assumed rate of generation of heat in Fig. 8, $q = 1 \times 10^{-7}$ calorie/sq cm/second, is equal to 3.16 calorie/sq cm/year, which according to the preceding result, is the equivalent of $3.16/0.3609 = 8700$ feet of granite beneath the sediments. This rough calculation shows from Fig. 8 that excess of radium in granite may add several degrees to the temperatures in sediments arched up over granite domes or ridges.

Conversely, it may be possible to reverse the process and from the data given by geothermal and subsurface surveys, obtain values of q_g and q_s, the respective rates at which heat is generated in granites and in the overlying sediments.

Thus, Fig. 11 shows roughly the relation of three isogeotherms in central

Oklahoma to the upper surface of the basement rocks. The isogeotherms can be used to evaluate q_g and q_s; but, for simplicity in illustration, let it be assumed that the temperatures (θ), at constant depth x_1 have either been observed or interpolated for the points d_0, $d_1 \ldots d_n$.

Evidently, the excess heat developed in the granite at $d_0=0$; at d_2, it is proportional to *ab*; and for convenience we can assume that this heat is generated on a plane passing through *f*, the mid-point between *a* and *b*. Now from diagrams like Fig. 8, the rise in temperature for each point *d* can be obtained. Let us call these temperatures, $\theta_1', \theta_2', \ldots \theta_n' (\theta_0'=0)$. Similarly, let $\theta_0'', \theta_1'' \ldots \theta_n''$ be the values computed in the same way from the sedimentary columns. And, furthermore, let a_0=annual mean temperature of the soil at 0 depth; b_0=gradient at the origin; β=coefficient of variation of gradient with distance from the origin, such that the calculated temperatures, independent of radioactive heat, are given by $\theta_n=a_0+x_1b_n$ $=a_0+x_1(b_0+\beta d_n)=a_0+x_1b_0+x_1d_n\beta$. Then the equations to be solved are of the type

$$a_0 + x_1b_0 + x_1d_n\beta + \theta_n' + \theta_n = \theta_n \qquad (2)$$

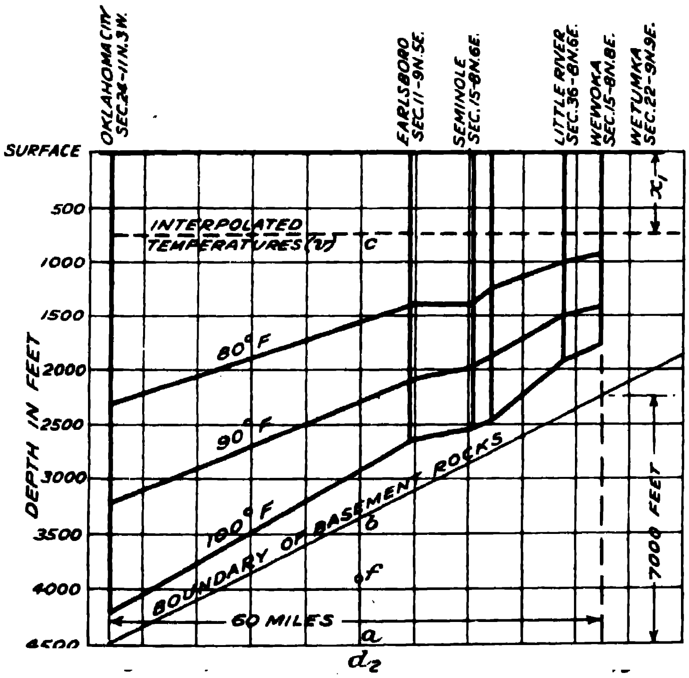


FIG. 11. Isogeotherms in central Oklahoma and superimposed sketch showing approximately the relation of the isogeotherms to the basement rocks.

In solving Equation (2) it is necessary to assume a value of q_g and then compute the temperatures for a series of values of q_s. Repetition of the process for a series of values of q_g will enable one ultimately to select a pair of values of q_g and q_s which minimizes the sums of the squares of the residuals and thus gives the required values of the constants.

The application of correct mathematical theory to this problem should lead to rather precise determinations of the constants. Especially is this true in exceptional domes like Salt Creek, and synclines, like the northern end of the Appalachian trough where the height of the granitic mass in New York above the general level of the basement rocks in Pennsylvania and West Virginia amounts to more than 17,000 feet.

Summary

The mercury maximum thermometer is a very useful instrument in the oil fields, but it will ultimately be displaced by electrical thermometers when suitable cables can be constructed at a reasonable cost.

Standardization of units and methods of representation of data are needed.

From the evidence presented in this paper, it seems that temperatures in oil fields are dependent largely on four factors: (1) Configuration of the strata; (2) thermal conductivities; (3) depths of basement rocks; and (4) sequence of geological events.

Radioactivity may cause a small part of the changes in temperature over anticlines, in synclines, or along regional dips.

It may be possible to evaluate the rates at which radioactive heat is generated in sediments and basement rocks, using the data of geothermal and subsurface surveys.

Thermal constants can probably be best determined by measurements in the field and laboratory. As the data of geothermal and subsurface surveys, however, provide an unlimited number of observation equations, it may be possible to evaluate these constants together with the constants of radioactivity.

Note on Temperature Survey of Nesa 11, Long Beach, California

I am greatly indebted to Dr. A. S. Baptie, Geologist, Shell Oil Company, for his kindness in making the necessary arrangements for me to test this well of such exceptional depth. In making the test, the set of three thermometers, Fig. 1-F, was enclosed in a tube used in making bottom-hole temperature and pressure surveys. The tube was handled as is usual in the oil fields on a Halliburton line. Small pieces of cotton placed above and below the thermometers prevented oscillations of the thermometers within the tube. Electric power was used. Mr. George Young of the Shell Oil Company operated the Halliburton line. As a final check on the readings, two runs were made to 9000 feet. The difference between the two sets of readings, using a different set of thermometers on the second run, was less than 0.2 °F.

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Temperature in Oil Wells

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Introduction

Temperature observations in oil wells have usually been in the nature of incidental data gathered in drilling or producing operations. In very few instances has an independent study been made of the subject for its own purposes.[1,2,4] However, the continuous penetration to deeper levels in recent years has focused attention forcibly upon the question of temperature because of physical difficulties and material failures. The scientific need for temperature information has been emphasized by the rapid advance of reservoir mechanics through applied thermodynamics, physical chemistry, and laboratory technic.

Production

In normal producing operations, subsurface temperatures are mostly gathered as a means of correcting the indications of subsurface pressure recorders. Occasional observations are obtained in conjunction with special studies of bottom-hole sampling, flow-tube conditions, and water location behind casing. These values may be accurate within plus or minus two degrees, but are not always properly qualified by supplementary information. More important practical difficulties reported to date include critical deterioration of leather, fabric, rubber, or composition packing materials; excessive differential expansion in parts of equipment made from varied metals; critical effect on some chemicals and solvents used in sealing water-sands and removing deposited wax; excessive temperatures of tank oil at higher flow rates with attendant gravity loss; and serious insulation troubles on submersible electric pumps.

Drilling

Mud fluid circulated in deeper and hotter holes has been showing still more increase in surface temperature since greater rates of circulation have been employed with smaller closed screening circuits at the derrick. In some cases the temperature of mud returns has been high enough to reduce volumetric pump efficiency materially. The decomposition temperatures of several mud-stabilizing chemicals have also been reached. This aggravates the known tendency of mud to increase its viscosity and water loss at elevated temperatures.[11,12] Some competent engineers also hold the opinion that extreme mud temperatures may adversely affect the cutting action of the bit. In any case, mud control and good performance must be maintained to prevent loss of valuable open hole. Several wells in California have successfully carried about 11,000 feet of uncased hole, and one project is now exploring beyond 14,000 feet with less than 1000 feet of surface casing.

Successful cementing operations, without which no well is completed, depend upon a knowledge of hole temperatures and selection of suitable cement whose properties will permit sufficient setting time under the accelerating effect of high temperature. The complex problems of heat transfer and temperature changes in this problem are the subject of special study by a committee under sponsorship of the American Petroleum Institute. Materials which have caused trouble because of the higher temperatures include synthetic rubbers and packing compositions, alloys whose expansion coefficients vary markedly from that of steel, film and dry-cell batteries used in surveying instruments, and insulation on electrical conductor cable. In a very recent case, insulation or packing failure prevented proper functioning of a resistance thermometer and precluded gathering of important temperature observations in a 14,000-foot test well. A maximum-registering mercury thermometer indicated 308 °F at a depth of 13,980 feet.

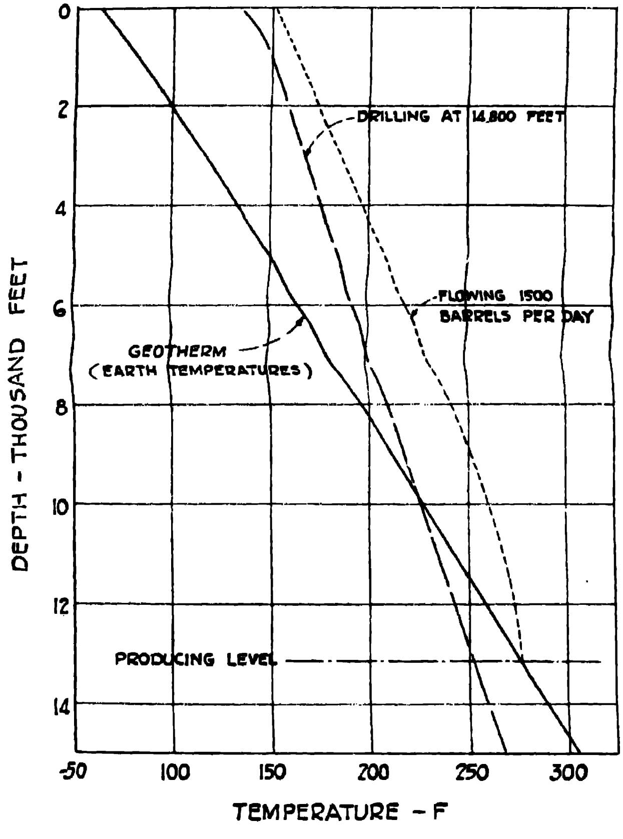

FIG. 1. Deep-well temperatures.

Deepest Well Temperatures

The temperature relations in a deep well and the difficulties of obtaining and qualifying observations are illustrated in the case of the 15,004-foot well referred to in Fig. 1. Attention was directed to the effect of elevated temperatures in this project when film melted in the surveying instrument used to record deflection of the hole. Batteries also were melted in some surveying devices, even though they were packed in Dry Ice. At lower depths it was found that maximum-registering thermometers could not always be relied upon because of shakedown caused by the severe vibration to which the instrument was subjected during the round trip. Fusible plugs graduated as to melting points yielded good results for temperature maxima. The continuous-recording resistance thermometer run on a conductor cable gave a satisfactory traverse, and information on the change of mud tempera-

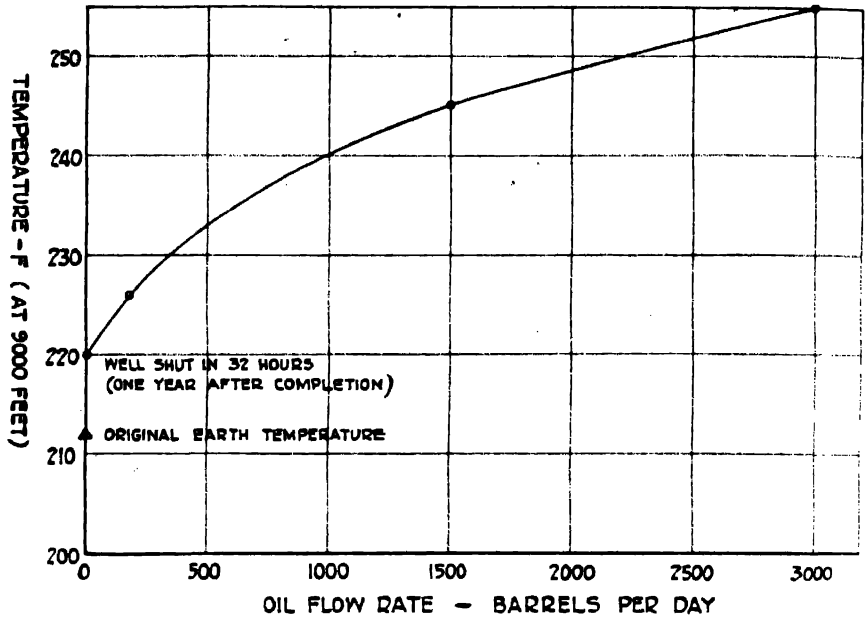

FIG. 2. Temperature variation with flow rate 4100 feet above producing horizon.

ture following cessation of circulation[8] (11,500 feet) was provided by an instrument which continuously photographed the dial of a laboratory-type indicating thermometer.

The solid line in Fig. 1 represents the approximate geothermal gradient for the field. The broken line shows mud temperatures as determined five to seven hours after cessation of circulation. These clearly portray the cooling of the lower portion of the hole, and the warming of the upper levels by the mud which is pumped down through drill pipe and returned in the annular space. The relative displacement of this line from the solid line depends primarily upon rate of circulation and the amount of surface cooling the mud received. After completion of the well, and recovery of formation temperature at the producing interval, little change is noted unless intrusion of water, oil, or gas in large quantities from higher or lower horizons takes place. However, temperatures above the producing level may be raised tremendously during higher rates of flow, as shown by the dotted line in Fig. 1, as well as by Fig. 2. Time is still another variable, and many cases have revealed the effect of heat transfer from hot oil rising through the earth. Upper horizons may be raised very appreciably above their true earth temperatures, and the period necessary to regain complete equilibrium may become very long indeed. Fig. 2 gives indication of such heating effect at 9000 feet where the temperature, after 32 hours of shut-in period, is still unmistakably above the natural earth temperature. The data upon which this curve is plotted were obtained after the well had been producing an average of 300 barrels per day for about one year.

Geological Aspects

Aside from their use to the petroleum producer, qualified temperature data hold many valuable clues to the geological history of glacial epochs, climatic changes, effects of vulcanism, and other phases of the earth's development.[2,3,9] Variance of geothermal gradients in California is indicated by the differences in depth at which approximately 175 °F is reached in different fields.[8] In some areas this temperature is reached 3200 feet below the surface, in others at about 7200 feet; and differences in surface mean temperature, surface elevation, etc. do not account for the disparity. Local opinion points toward the variation in thermal conductivity of the rocks and relative proximity to the basement complex as the most important factors.

Summary

Operating problems caused by higher temperatures will no doubt be solved as more attention is directed to them, and as their occurrence becomes more frequent. There is a present need for more dependable and sensitive thermometers, of both the maximum-registering and continuous-recording types.

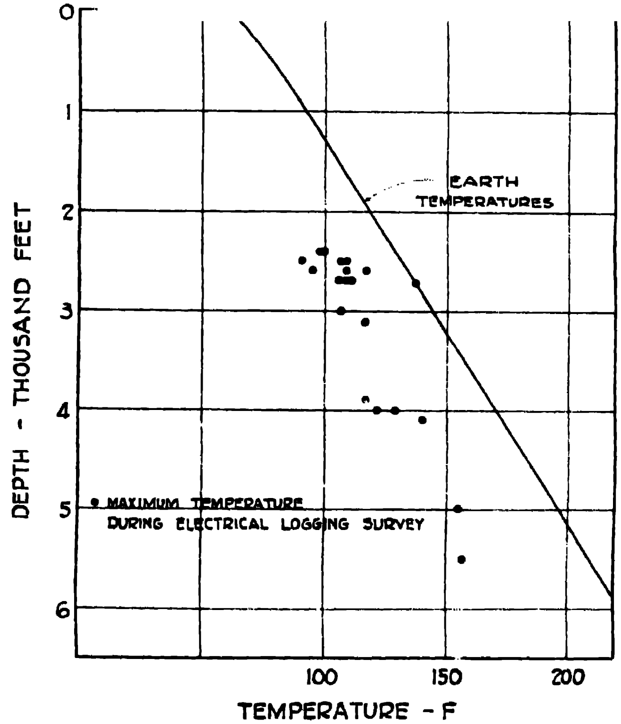

Fig. 3. Effect of recent mud circulation on bore-hole temperatures.

It must be more generally realized that a producing well is a cause of considerable heat transfer, and that random temperature determinations are useless or misleading unless qualified by supporting data. In the case of the drilling well the concept of temperature equilibrium must also be applied in qualifying thermometer indications, as demonstrated in Fig. 3. These points were taken from the files of an electric logging service and show the wide dispersion of temperatures unclassified as to history of recent mud circulation. Such data are practically useless for estimation of true earth temperatures.

The study of accurate geothermal gradients, combined with investigation of the pertinent geological background and supplemented by diffusivity and density determinations, should not only prove an interesting field for scientific groups, but also a worthwhile project from the industrial standpoint.

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Temperatures as Affecting Oil-well Drilling and Production

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This report deals primarily with the effects of temperature encountered in drilling and producing oil and gas. No attempt will be made to review every phase where temperature affects drilling and production. Only those cases wherein temperatures have an influence from an economic standpoint and in which these effects are dealt with scientifically will be discussed.

I. Temperatures Affecting Oil-well Drilling

From the surface to depths as great as 13,000 feet the changes in temperatures that are encountered have a decided bearing upon drilling technic and supervision, and equipment used in oil-well drilling. There are cases on record where the total loss of a drilled hole was attributed to the existing earth temperature at great depths. Some of the most important effects of temperatures under drilling conditions are briefly discussed below.

(1) Rotary Drilling Fluid

One of the most important effects of temperature upon drilling is the effect of increased temperature on drilling mud, such as:

(a) Effect of Temperature Variations on Mud Weight or Density. Increasing the temperature of drilling mud slightly lowers its density; however, this effect is negligible in ordinary cases. At its boiling point, the density of water is only 4 per cent less than at the freezing point, and this slight variation is of minor importance.

(b) Effect of Temperature Variations on Drilling Mud Viscosity.[1] Drilling muds usually exhibit a minimum viscosity at some point in the range 100 to 140 °F, but muds are not entirely consistent in this regard. At high temperatures, chemical mud thinners are less effective, and their effect shorter lived than at low temperatures. This makes viscosity control generally much more difficult when the muds are hot.

(c) Effect of Temperature Variations on Wall-building Properties of Drilling Muds. Increased temperatures invariably increase the cake thickness and volume of water filtering from the mud into the formations.[2] This effect is due to two causes. First, the rate of filtration varies inversely as the square root of the viscosity of the filtrate (water). Increased temperature decreases the viscosity of the filtrate from mud, and hence increases the total amount of filtration as measured by cake thickness and volume of filtrate. Secondly, increasing temperature generally results in increased solubility of slightly soluble mud-flocculating materials in water. An increase in the amount of dissolved material increases the flocculation of the mud, and this results in poorer wall-building properties.

Summing up, increased drilling mud temperatures usually add to the problems of mud control by increasing the mud's viscosity, hence making viscosity control more difficult and also decreasing the effectiveness of the mud in its wall-building operations in the hole.

(2) Rotary Drilling and Coring Bits

Very few studies have been made on the effect of drilling bits while drilling in various types of formations; or, if such studies have been made, the writer has not been able to obtain access to the data. However, it has been observed by major tool companies who manufacture drilling bits that temperatures in excess of 350 °F would, in all probability, reduce the effectiveness of rock and core bits.[12] The exposure of the toothed cutters in roller bits designed for drilling hard formations to temperatures of 350 °F and above will soften the case-hardened structure and probably result in an inferior performance of the bearings.

Based on observation, however, it is the opinion of the writer that the temperature of bits resulting from friction in drilling a hard formation with 6000 and 8000 lbs weight on the bit will be far in excess of 350 °F. Although the drilling mud helps greatly in keeping the bit cool, the high friction temperature is perhaps the principal reason for a case-hardened rock-bit drilling less than 10 feet of hole in extreme cases.

(3) Rotary Drill Pipe and Tool Joints

In present drilling to depths of 13,000 feet, the temperature effects on drill pipe and tool joints will not impose any additional limitation on the safe use to which this equipment can be exposed. It is reasonable to assume that 350 °F will not adversely affect our present drill pipe and tool joints, and it is doubtful that temperatures as high as 350 °F will be encountered until depths of 15,000 feet to 20,000 feet are reached.

(4) Cementing Operation in Rotary Drilling.

Only recently have high bottom-hole temperatures seriously impaired cementing operations. With shallow wells, the ordinary oil-well cement was entirely satisfactory, and until as late as 1936, there was no need for an especially prepared slow-setting oil-well cement. When drilling depths increased to below 6000 feet, the bottom-hole temperatures of 150 to 170 °F that were encountered rapidly increased the setting time of ordinary cement. This fact, together with the additional delay in pumping cement through 6000 feet or 7000 feet of casing, has been directly responsible in several cases for the cement setting inside the casing and becoming immovable before only a small part had passed out through the casing shoe, thereby improperly cementing the hole and causing unnecessary delay in drilling out several hundreds of feet of cement in the casing.

As an actual early example where temperature caused the operators considerable trouble in the process of cementing a hole was in July, 1936, where 2000 sacks of straight portland cement were mixed and pumped into a string of 7″ casing 10,900 feet deep. The plug was put in and pressure applied; the cement moved down 3000 feet at which point it was impossible to move it farther. This left 7900 feet of cement in the pipe and very little on the outside. The gradual rise in pressure up to the point where the cement became immovable proved beyond doubt that the high bottom-hole temperature caused the premature setting of the cement.[14]

The increase in bottom-hole temperature as wells were drilled deeper made it imperative that improved cements be developed.[3] Bottom-hole pressures up to 5700 pounds and bottom-hole temperatures as high as 335 °F have been encountered in deep-well cementing operations.[27] To meet this condition, a cement now has been made available to the oil industry that will remain pumpable at temperatures higher than 212 °F and will remain in a movable state at these temperatures for more than 2 hours.[13] As a typical example, with a bottom-hole temperature of approximately 250 °F, there have been no cement failures reported for any of the wells completed in the California Wasco Field where production is obtained from a 13,200-ft horizon. In 1936, the success of the Gulf Oil Corporation's McElroy Well in West Texas in reaching a record depth of 12,786 feet was partly due to the comparatively low bottom-hole temperature of 182 °F.[28] Not only does the high earth temperature increase the setting time of cement, but investigations by Jessen and Webber[8] show that a 40-per cent slurry (ordinary oil-well cement mixture) reaches a maximum temperature of 150 °F.

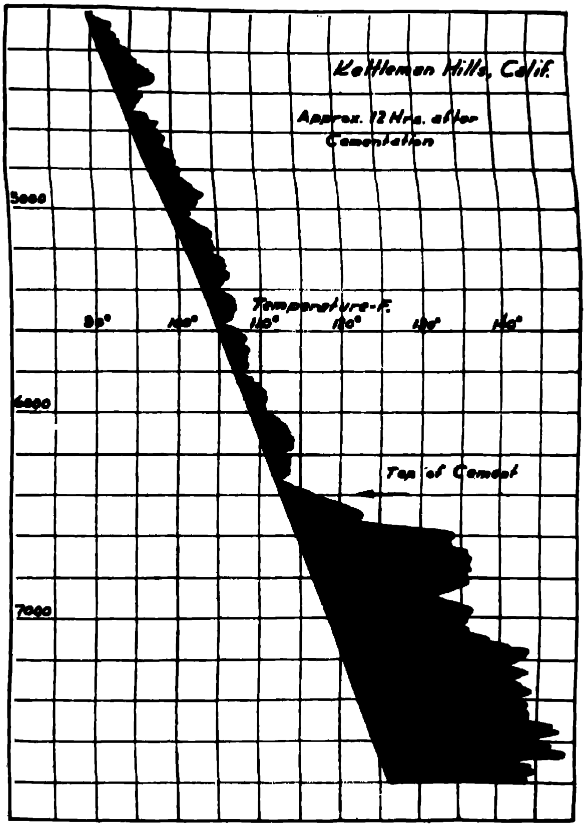


FIG. 1. Reproduction of Fig. 1, p. 793 in Vol. 21, Bulletin No. 6 of the American Association of Petroleum Geologists, "Use of Temperature Measurements for Cementation Control and Correlations in Drill Holes," by Alexander Deussen and Hubert Guyod.

(a) Location of Cement behind Casing by Temperature Measurements. In interpreting the data obtained by electrical temperature surveys, the assumption must be made either that the fluid in the well and the surrounding area is in thermal equilibrium, or that the fluid in the well and the surrounding area is *not* in complete thermal equilibrium.

Casing in oil wells is cemented for various reasons, the principal one being to effectively seal off upper sands to prevent the intrusion of water from formations above the oil zone. The amount of cement required is calculated theoretically as a function of the size of the casing, the size of the hole and the height outside the casing the cement is expected to reach. But the hole may be far from regular, some porous sands may absorb the slurry and channelling may also occur. Thus knowledge of the exact location of the cement is of prime importance when there is any doubt as to the success of the cementing operation.

The principle of the temperature surveys is based, not on earth temperature, but on temperature from the heat of hydration during the setting process of the cement, assuming that the fluid in the hole and the surrounding area is not in thermal equilibrium, but only the area immediately in contact with the casing. Temperature surveys of deep wells are made from a power hoist mounted on a heavy-duty truck and with sufficient cable to make a 15,000-ft survey. The instrument itself consists of a resistance thermometer with a surface recorder giving a continuous record of temperature changes as the instrument is lowered into the hole. Temperature surveys to determine the location of cement behind casing are best made within 24 hours after the cementing process. This will allow ample time for the fluid in the hole to reach a state of thermal equilibrium with the setting cement and also prevent the heat of hydration from being completely

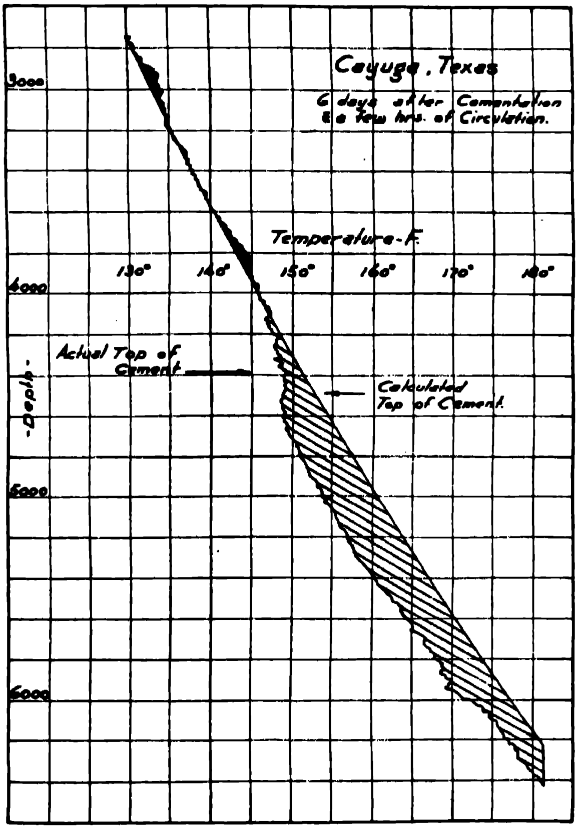


FIG. 2. Reproduction of Fig. 6, p. 799, Vol. 21, No. 6, Bulletin ot American Association of Petroleum Geologists, "Use of Temperature Measurements for Cementation Control and Correlations in Drill Holes," by Alexander Deussen and Hubert Guyod.

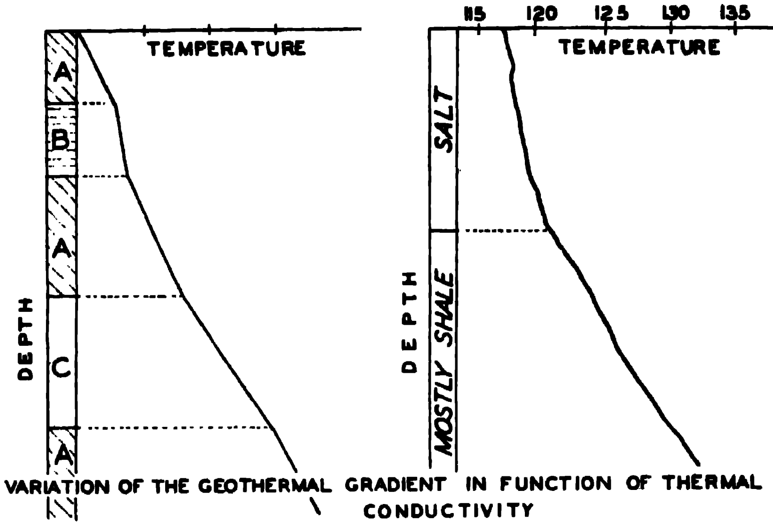
absorbed by the formations. Fig. 1 [15,16] is a record of an actual survey in a 7800-ft well in Kettleman Hills, California, to determine the top of the cement. The run was made 12 hours after cementation and the sharp increase in temperature at 6350 feet clearly indicates the top of the cement outside the casing.

It is possible, although at present there are no actual cases on record, that in a deep well below 12,000 feet where the earth temperature is greater than the heat of hydration of the setting cement, the temperature curve would tend to show a decrease at the top of the cement rather than a sharp increase.[15] Thus far, the nearest approach theoretically to this condition is illustrated in Fig. 2.[15] The well is more than 8700 feet deep. Casing was set at this depth and cemented with 350 sacks. In addition, another 350 sacks of cement were squeezed through perforations at 6635 feet. The cement mixture was made using 10 tons of ice as a cooling medium, the final temperature being 40 °F. In the opinion of the persons in charge of the temperature survey, the sharp negative anomaly below 4400 feet was due to the presence of the cool cement below that level not having completely reached a state of thermal equilibrium with the surrounding area.

(5) Electrical Temperature Logging with Survey Instruments.

In the discussion of the location of water and gas-oil flows and the correlation of drill holes by recording subsurface temperatures, it is of interest to first consider the progress and development that have been made in the investigation of the temperature anomaly existing in oil wells at great depths. Full credit for evolving a suitable method and operating technic, as well as for designing the practical apparatus which has made the thermometric measurements possible, should go to Messrs. C. & M. Schlumberger and H. D. Doll.[4] The first instruments used in measuring temperature in oil wells and mine shafts consisted of a series of thermometers attached at intervals along a cord and lowered into the hole. These thermometers could be withdrawn at periodic intervals and readings made to determine the temperature changes. Another early instrument was commonly known as a "Single-Shot"; simply a single thermometer lowered to a desired depth, allowed to remain until a state of thermal equilibrium was reached, and then withdrawn. Thus we see that extensive measurements were hampered by the lack of a suitable and practical instrument and consequently of an adequate operating technic. Such an instrument has now been evolved and has been in actual field service for the last few years, whereby the maximum amount of data can be had by tracing a continuous temperature log over the entire depth of the hole in a sufficiently short time. This instrument is based on the well-known phenomenon of the variation of the electrical resistance of a conductor as a function of its temperature. The Wheatstone bridge principle can be used, and it will readily be understood that a potential difference measurement can be substituted for that of the resistance, and correlated to give temperature readings. The accuracy with this method can reach 0.2 °F, and the "time constant" is such that continuous logs can be traced at the satisfactory speed of approximately 2000 feet per hour without any appreciable lag.[5]

(a) Correlation in Drill Holes by Means of Sub-surface Temperatures. To some extent, the logging of geological strata traversed by a drill hole is feasible by means of temperature measurements. Because of the high thermal conductivity and heat capacity of the fresh-water- and salt-water-bearing sands, the rate of exchange of heat between the mud or fluid in the hole and the formations, after circulation has been stopped, is much larger opposite these sands than opposite shales.[15] Thus a temperature curve made a few hours after circulation has ceased should therefore show temperature changes at each formational contact. In the earth's crust, thermal conductivity varies with the nature of the rocks. For



FIGS. 3 and 3A. Reproduction of Fig. 1, p. 3, "Temperature Measurements in Oil Wells," by M. Schlumberger, H. G. Doll and A. A. Perebinossoff, Institution of Petroleum Technologists.

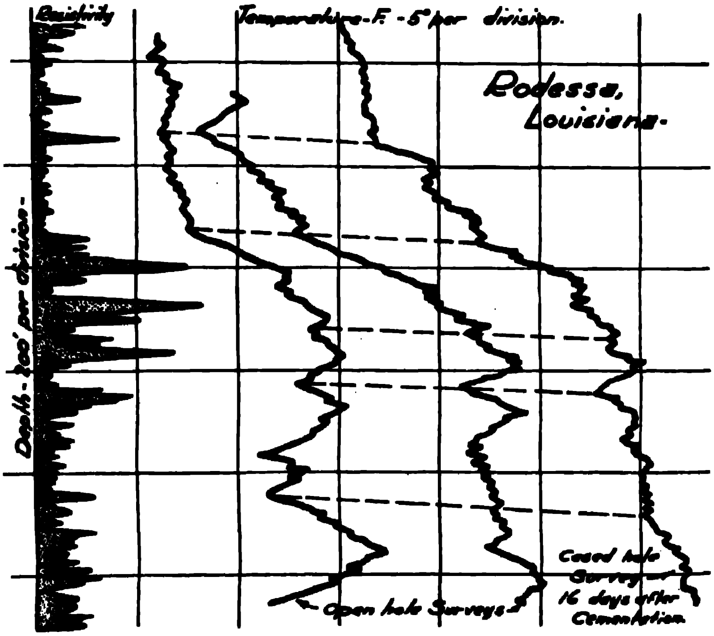


FIG. 4. Reproduction of Fig. 11, p. 805 in Vol. 21, No. 6, Bulletin of American Association of Petroleum Geologists, "Use of Temperature Measurements for Cementation Control and Correlations in Drill Holes," by Alexander Deussen and Hubert Guyod.

instance, a dry sand may have a conductivity of 3.10^{-4} gm. calories/cm^8/°F. Oil may have the same conductivity. The conductivity of ground water varies from 14.10^{-4} to 66.10^{-4} or more.[4] Thus it can be seen that the variation of the geothermic gradient will be closely related to the succession of rocks encountered, and will mark the important stratigraphic changes. Fig. 3[5] illustrates this condition theoretically and Fig. 3^a[5] is a practical illustration of this example.

Fig. 4[15] is an example of correlation between three wells at Rodessa, Louisiana. Although it is quite evident that temperature measurements in oil wells are far from being capable of giving the accurate and complete information which the electrical resistivity and porosity logs now give in correlation work, the three examples illustrated in the diagram show that in some cases such measurements can be used to correlate wells already cased, where no other method of investigation is pos-

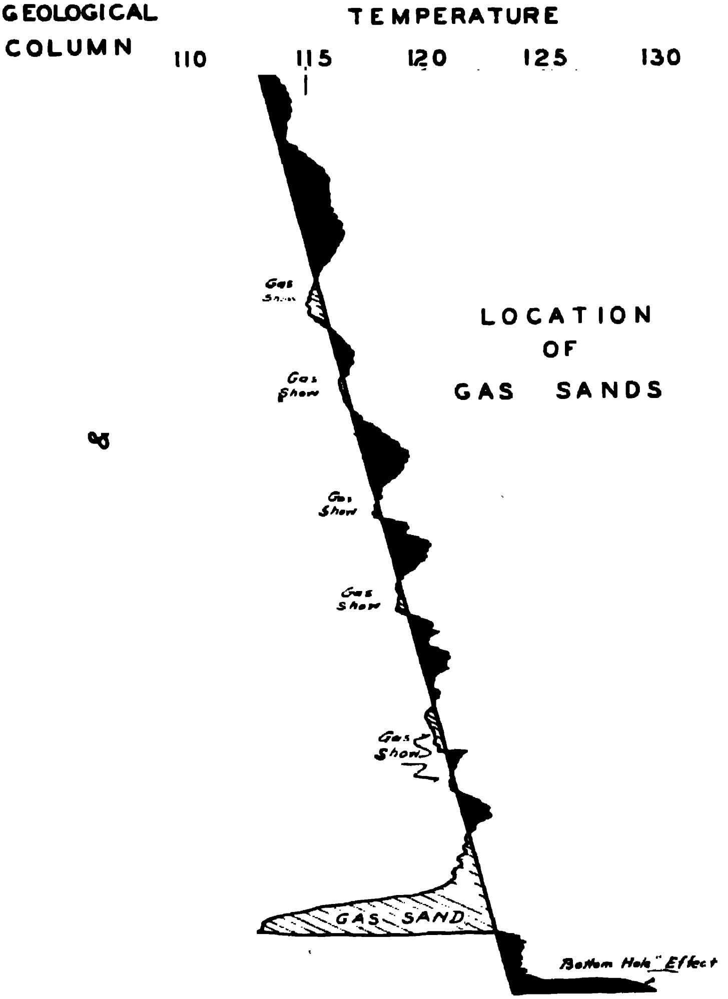
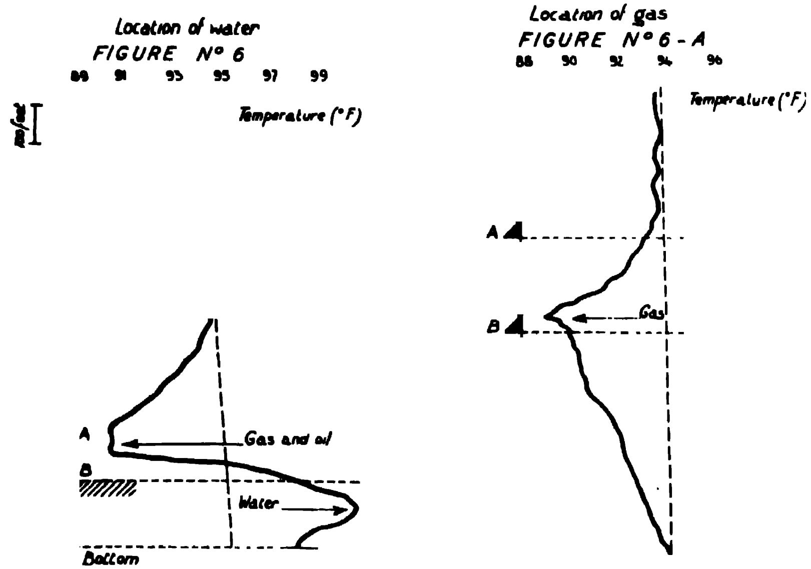


FIG. 5. Reproduction of Fig. 3, p. 8, "Temperature Measurements in Oil Wells," by M. Schlumberger, H. G. Doll and A. A. Perebinossoff.

sible. Although the example in Fig. 4 shows strikingly the different formations traversed by the hole, the problem of logging formations by temperature measurements has proved difficult in many cases. In fact, many temperature curves show abnormalities which seem to be without apparent relation to the stratigraphy of the formations.[15] Also, many geological markers, or "tops," although definitely revealed by the electrical porosity logs, do not appear clearly on the temperature curves. However, it is expected that, in the future, as improvements are made and more knowledge is gained by work with temperature survey, considerable more information will be made available by these measurements and investigations.



Figs. 6 and 6A. Reproduction of Fig. 5, p. 11, "Temperature Measurements in Oil Wells," by M. Schlumberger, H. G. Doll and A. A. Perebinossoff, Institution of Petroleum Technologists.

(b) Location of Gas-oil and Water Flows. The location of gas-oil and water flows by a temperature survey is not based solely on the natural convection movements. Here is an example of the importance of the assumption that the fluid in the hole and the immediately surrounding area is in thermal equilibrium. If the sands are being produced in neighboring wells, or in the well under investigation, they will be cooler than the formations above and below because of gas expansion, or as the case may be, warmer in the event of water movement.

As shown in Fig. 5,[5] a temperature survey will accurately locate a gas-oil-bearing formation. The gas, together with oil, bubbling out of the hole during drilling, or being produced if a production test is made, will cool off the formation at the point where it enters the hole, the cooling effect being due, of course, to the expansion of the gas upon entering a region of reduced pressure.

(c) Economic Importance of Temperature Measurements. A practical example of the economic importance of accurately locating gas and water flows is illustrated in Figs. 6 and 6a.[5] The first example concerns the location of intruding water after casing had been cemented at the point *A*. From the results of the temperature survey, the well was plugged to the point *B*, reducing the water cut to less than 1 per cent. The second example, Fig. 6a, refers to the location or determination of gas entering in a cased hole. This well was completed with casing set at the point *A* and allowed to produce by natural flow for a period of two months. From the very beginning, the gas-oil ratio was high; but, as production continued, it increased even more. The decrease in temperature, as shown on the temperature curve, clearly indicates the point at which gas is entering the well and the persistence of the low temperature below the obvious point of greatest entry, even suggests that some gas may have passed downward and was gradually excluding the flow of oil. Following the temperature survey, an insert liner was cemented at the point *B*, and the well was again completed as a good producer with a low gas-oil ratio.

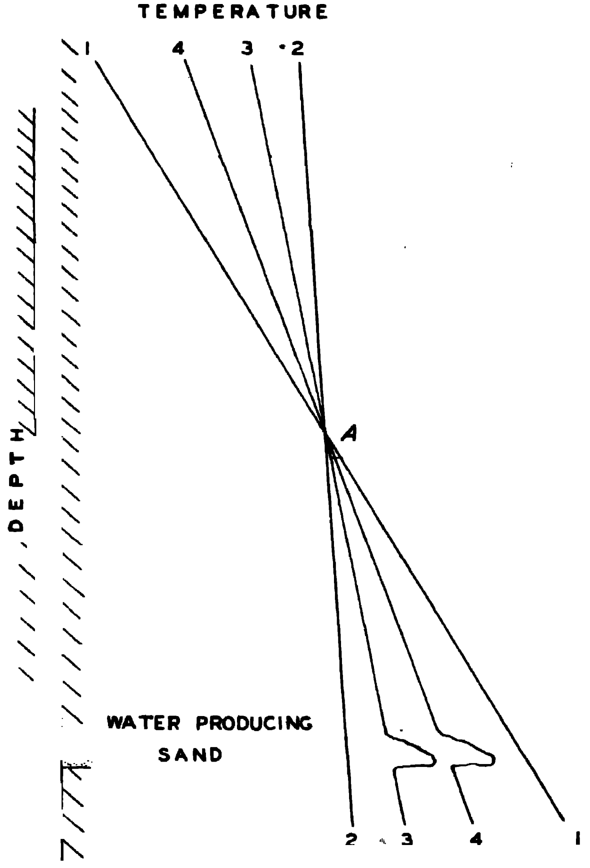


FIG. 7. Reproduction of Fig. 2 in a reprint from *Oil Weekly* (June 29, 1936), "Location of Water Flows in Drill Holes by Temperature Measurements," by H. Guyod, Houston, Texas.

To define the point of entry of a water flow into the hole requires considerably more time and effort than to locate the entry of gas-oil flows. In Fig. 7,[6] let us suppose that the well to be examined is filled with water or mud and that it has been kept idle for several days. A survey (first run) of the hole will give a temperature curve in terms of depth which will show approximately the geothermal gradient of the formations (Curve 1). If the mud is then circulated a few hours, the equilibrium of temperature between the mud and the formations will be destroyed. A temperature survey (second run) made after this circulation will give a similar curve (2) crossing curve (1) at point *A*. Let us suppose now that the water to be located comes from the lower part of the hole. If, after the second run, the hydrostatic level of the well is decreased (for instance, by bailing a certain quantity of fluid), in order to produce a small flow of water into the hole which has about the same temperature as the formation from which it comes, the incoming water will be warmer than the fluid which it has displaced in the hole. A temperature survey (third run) made immediately after bailing will give a curve similar to curve (3), showing a peak at the level at which water is entering the well; curve (4) is a survey to check curve (3).

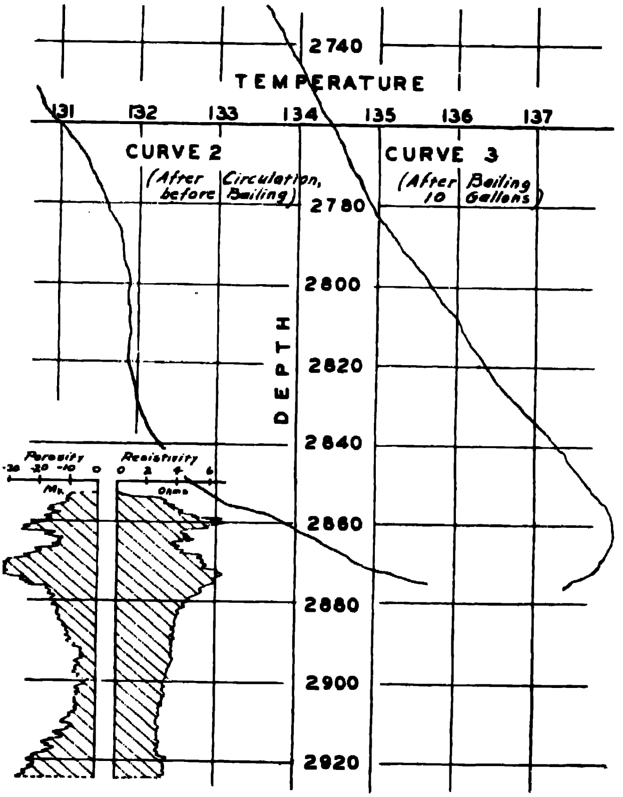


Fig. 8. Reproduction of Fig. 3 in a reprint from *Oil Weekly* (June 29, 1936), "Location of Water Flows in Drill Holes by Temperature Measurements," by H. Guyod, Houston, Texas.

Referring to Fig. 8[6] for an actual example, curves (2) and (3) correspond to the second and third runs described above. They indicate that the water is coming from 2856 feet to 2866 feet. This interpretation conforms, by the way, to the results of the resistivity and porosity diagrams which are also plotted on the figure.

Of course, the thermometric technic of solving water-flow problems is a quite recent development and can be improved after a large number of surveys have been made under various conditions. Nevertheless, the writer feels that the results already obtained are more than encouraging and are of sufficient interest to be included in this report.

II. Temperatures Affecting Crude-oil Production

In recent years, there have been numerous reports published on the conservation of natural reservoir energy, namely pressure, for the efficient and economical production of crude oil. Also, in these reports, it is generally assumed that the reservoir energy, in the form of heat, will maintain practically constant temperatures, regardless of the rate of withdrawal. Thus far, to the writer's knowledge, the study of the effects of subsurface temperature on the flow of oil and gas through the sands has been sorely neglected. Consequently, because of insufficient data concerning the effect of temperature upon formation drainage, only the condition in which temperature affects production at the surface will be discussed.

(1) Flowing Production

Solar heat is the principal factor to be considered in a discussion of the effects of temperature on production. In the Maracaibo Basin, Venezuela, were it not for the fact that the year-round temperature seldom drops below 85 °F it would be impossible to produce some of the wells completed in the shallow tar sands. Gravity of the crude from these wells is extremely low, ranging from 9° to 14° A.P.I., and if allowed to drip out on a flat surface, the oil will actually appear to "stack up." Thus we see the impossibility of attempting to transport this grade of oil through pipe lines at temperatures even as low as 60 °F.

(a) Wax and Paraffin Deposits Affected by Temperature. Probably the best example of a typical paraffin-base oil is that produced in Pennsylvania. Certain oils produced in Oklahoma, Texas, and Mexico are of the "mixed-base" type; that is, an asphalt-base oil with traces of solid paraffin, or a paraffin-base oil with asphaltic products. Paraffin oils and the mixed-base type yield, on reduction to low temperatures, an appreciable proportion of light wax.[7] In wells having bottom-hole temperatures greater than 150 °F the accumulation of paraffin deposits in the tubing and flow line does not offer a serious problem during the summer months. However, as the surface temperature decreases, these wells need frequent clean-outs. Usually, several times a month the paraffin or wax deposits must be swabbed or scraped from the tubing and flow line to prevent complete stoppage of the fluid. Many ingenious methods have been devised to prevent paraffin accumulation by transmitting heat to the various lines during the winter months.

Several chemical compounds and mixtures for removing paraffin and preventing its deposition are on the market. They may be divided into two classes: namely, those that generate heat to melt the paraffin or increase its solubility in the oil; and those that act as a solvent to change the character of the wax, so that it will not crystallize when the temperature is decreased below its original melting point.[17] The first method is accomplished by the injection of caustic soda and aluminum filings which, upon the addition of water, react violently, generating about 700 B.t.u. per pound of mixture. This method, however, has the disadvantage of a high cost and often fails to accomplish the desired results, especially when used to remove paraffin from casing and tubing, primarily because most of the heat is liberated at the bottom of the hole instead of along the entire length of the tubing. To be effective, these chemical compounds and mixtures must be added continuously and allowed to remain in close association with the oil until the reaction is complete. In most cases, all the treated oil is removed from the well before any appreciable amount of paraffin has been dissolved.

A very efficient and practical method of eliminating paraffin deposits is found in equipping wells with steam coils; and at intervals, during which excessive paraffin has accumulated, a small portable boiler, capable of supplying superheated steam at a temperature above 500 °F and pressure of 1000 pounds, can be set up at the well and operated until the accumulation has been dissolved and passed into the tanks. This method is especially applicable to large wells that produce through tubing and are readily plugged with paraffin.[18]

Paraffin accumulations are removed from some gas lift wells by injecting steam with the input gas, either into the annular space between the tubing and casing, or into the tubing. The steam is usually injected at monthly intervals, or more frequently if necessary. Although steam gives satisfactory results in certain wells in which the condensate from the steam does not form an emulsion with the oil, it is undesirable to use in wells where the water and oil emulsify and require additional heat treatment for their resolution. One of the most satisfactory methods of removing paraffin accumulations from the eductor tubing in gas-lift wells involves heating the input gas in small heaters with steam. These heaters are not used continuously, but intermittently, whenever the accumulation interferes with production.[19] Similar heaters are also used to reduce the viscosity of oil from wells producing a low-gravity crude by the gas-lift method.

In summing up the various methods used for prevention as well as removal of paraffin accumulation we might add that methods are as varied as the types and kinds of accumulations. Only a few of the more common practices and methods of prevention and correction are enumerated above.

(b) Economic Importance of High Bottom-hole Temperatures. Bottom-hole chokes have recently presented a new application in connection with the operation of gas wells, since their installation practically disposes of freezing difficulties by utilizing the high subsurface temperatures more effectively.

An example of this application of bottom-hole choking to prevent freezing of surface control equipment, which is a serious problem in the operation of high-pressure gas wells, is shown in a 3000-foot well at Holdensville, Oklahoma.[21] The open-flow capacity was 14,000 M.C.F. with a closed-in pressure of 900 pounds. To supply the winter demand for gas, an elaborate system of surface heat exchangers was necessary. After the installation of a bottom-hole choke, the subsurface temperature of 185 °F was sufficient to prevent freezing, and the surface heaters were consequently abandoned.

Laboratory investigation of the effect of high temperatures and pressures upon the phase relations of hydrocarbon mixtures as they occur in deep sands (below 7500 ft) have been found to be rather consistent, and the products condensed from these deep reservoirs are likewise found to have a high distillation end-point. The amount of condensate obtained from the gas in these deep horizons varies from 0.6 to 3.5 gallons per thousand cubic feet; and it is a common, but erroneous, belief that a large portion of the crude oil at depths below 10,000 feet is in the vapor phase because of the extreme temperatures and pressures. Recent laboratory tests, however, indicate that it requires pressures well above 12,000 or 15,000 pounds, with a correspondingly high temperature, for the major portion of a 36°-gravity crude oil to pass into the vapor phase, and these conditions normally correspond to depths of wells in excess of 20,000 feet.[20]

In the Old Ocean Field, Brazoria County, Texas, when distillate production is obtained from a 10,000- or 11,000-ft horizon, the wells have a closed-in surface pressure of 3800 to 4000 pounds and an average temperature when flowing of 160 to 180 °F. This extremely high surface temperature results from the bottom-hole temperature of 215 °F,[22] and greatly increases the amount of distillate production when the gas-oil is allowed to expand to a lower temperature and pressure. Fig. 9[23] illustrates the procedure employed in designing a surface regulating valve for high-pressure distillate wells. Freezing is prevented by alternately regulating the pressure drop and using artificial means for increasing the temperature. Although the theoretical relation between temperature and pressure results in a ¾ °F drop in temperature for each pound of pressure drop in expanding gas, this chart is based on a decrease of 1 °F per pound drop in pressure to provide a safety factor in the design of a pressure-regulating system.

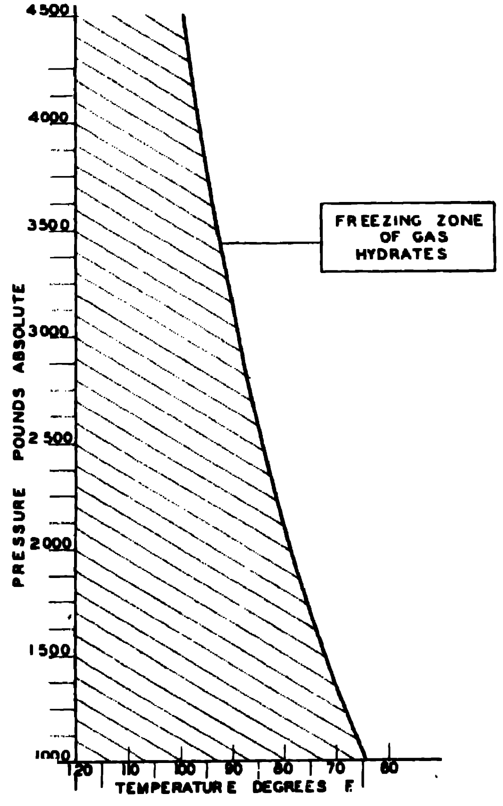


Fig. 9.

Reproduction of chart No. 2 prepared by Hanlon-Waters, Inc., Houston, Texas.

Temperatures below 0 °F to increase distillate production are very effectively used by one major company. In its re-cycling process, the temperature of the gas is reduced to −15° F without decreasing the well pressure, and requires a special brine solution to prevent freezing.[23] By this unique process, the distillate production has been increased 40 per cent above the ordinary expansion method, wherein the use of extreme temperature and pressure is disregarded.

In wells producing with a high gas/oil ratio and having well-head temperatures ranging from 120 to 140 °F, where the fluid is subject to extreme foaming, very efficient gas separation is attained by reducing the flow line temperature 40 or 50 °F before the fluid enters the separator.

(c) Heat Treating Crude-oil Emulsions. The percentage of water in emulsions that require treatment varies from 2 to 95 per cent in extreme cases. Some of the water ordinarily settles out on standing, but usually about 25 per cent of the water is so intimately united with the oil that treatment is necessary to effect a separation. Perhaps the most common type of treatment for water-oil is the use of heat alone; however, in a more stable emulsion, heat together with a chemical inhibitor is necessary.[8] The temperature to which the emulsion must be heated depends upon its character and will vary from 150 to 300 °F. Heat-treating tanks on "wet leases" are located between the well and the storage tanks and are usually equipped with steam coils. In this method, the water-oil enters through the bottom of the "gun-barrel" and as it passes upward outside the steam coils, separation occurs; thence the clean oil is allowed to flow from the top of the gun barrel by gravity into the lease storage tanks.

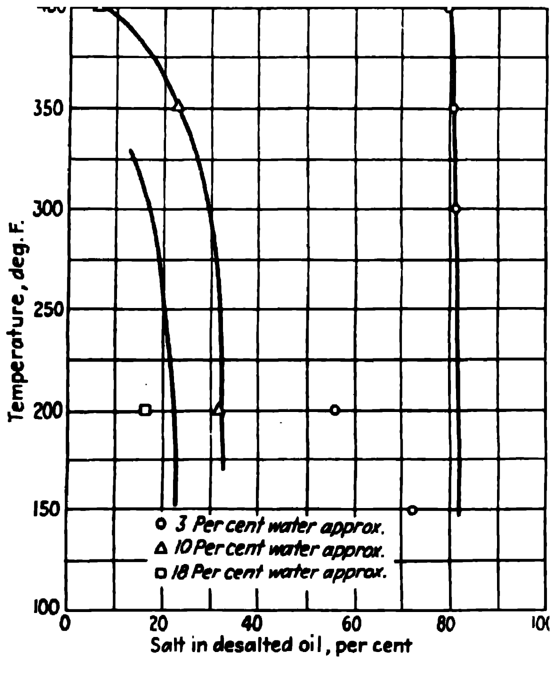


FIG. 10.

Reproduction of Fig. 2, p. 54 of the 1938 Petroleum Transactions, A.I.M.M.E. "Desalting Crude Oils," by Gustav Egloff, Edwin F. Nelson, C. D. Maxutor and Charles Wirth.

Extensive investigations have been conducted by Gustav Egloff and associates on the removal of salts and salt water from crude oils by heating.[9] It is estimated that of the 1,200,000,000 barrels transported by pipe lines in 1937, approximately 50,000,000 lbs were salts and 10,000,000 barrels were water. This amount of salt is derived from both salt water and crude oil. These figures fall well within the pipe line allowable of 1.5 per cent B. S. & W. It is needless to mention the harmful effects from corrosion that appear in refineries that handle these salt-containing crude oils. These investigations by Egloff and associates deal primarily with the more efficient treatment of crude oil at the producing leases and include suggestions for several practical methods. In this paper only the use of heat and the addition of water will be considered. The effects of temperature and percentage of water added on salt removal are closely related. From Fig. 10[9] Egloff and associates found that for the most efficient results, the addition of 10 per cent by volume of water with a temperature of 400 °F would remove all but 5 per cent of the salt in the crude oil. This, of course, is provided that the injection is made at the well and before the crude has "aged," permitting the formation of a more stable emulsion by the time the oil reaches the refinery. In the relationship of temperature and the percentage of water added, it was found that to obtain the same amount of salt removal for the addition of only 3 per cent water, the temperature would have to be increased to 500 °F. In general, the separation is poorest at 200 °F. and best at 400 °F. Fig. 10 is the result of intensive laboratory investigation.

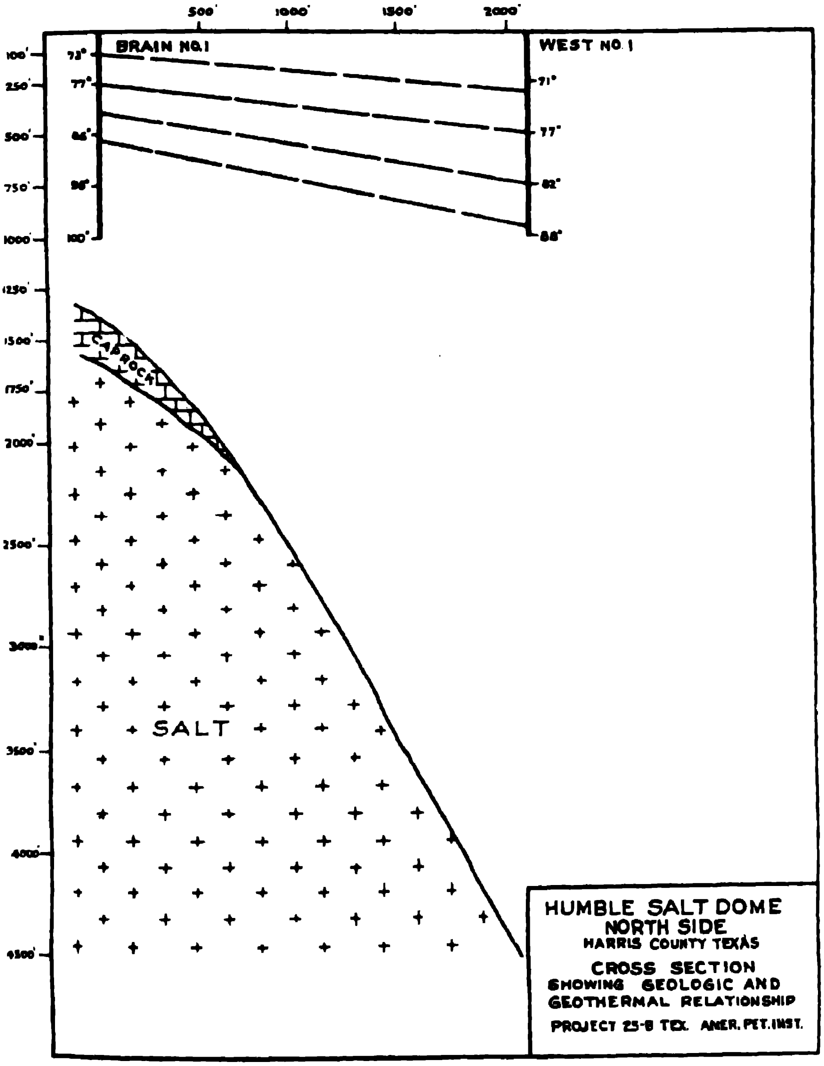


Fig. 11. Reproduction of Fig. 21, p. 79, A.P.I. Prod. Bulletin No. 205, "Results of Deep Well Temperature Measurements in Texas," by E. M. Hawtof.

III. Discussion of the Geothermal Gradient Present in the Gulf Coast Oil Fields

The American Petroleum Institute in 1936 inaugurated the first comprehensive study of the relation of geological structure in oil-producing areas and their geothermal gradients. C. E. Van Orstrand, who was placed in charge of this program, and others, have since written and published several interesting papers[24,25,26] on this subject. As a general rule, it has been observed that temperature increases with depth.

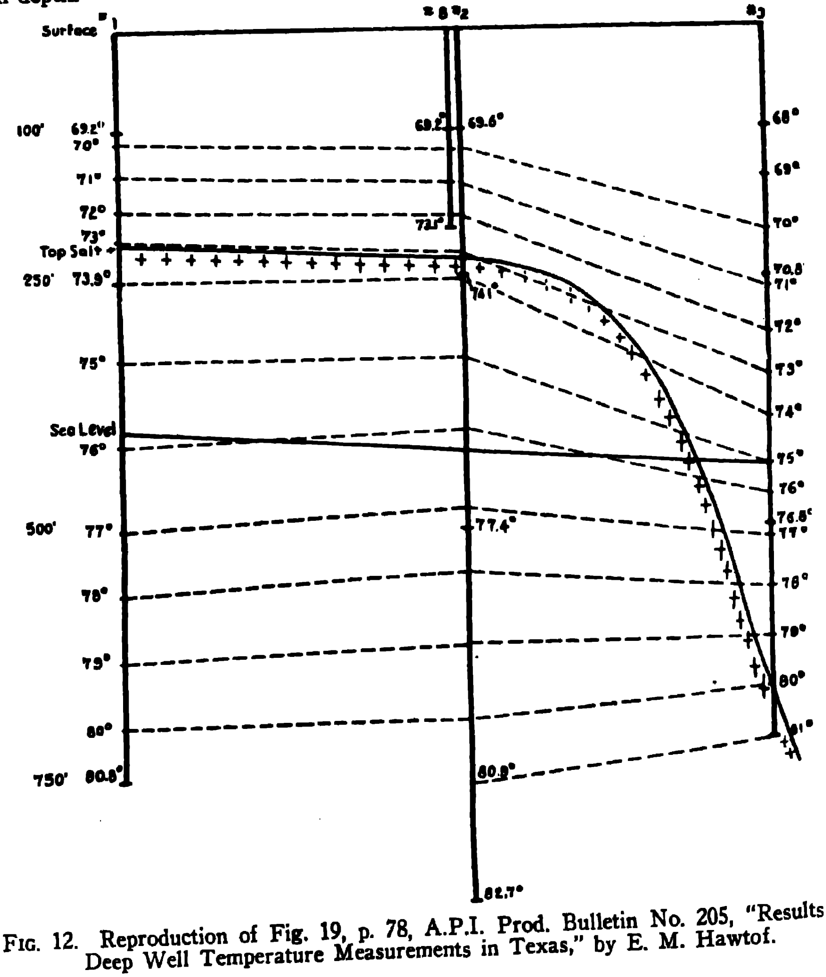


Fig. 12. Reproduction of Fig. 19, p. 78, A.P.I. Prod. Bulletin No. 205, "Results of Deep Well Temperature Measurements in Texas," by E. M. Hawtof.

(1) Importance of Temperature Surveys on Geological Structures

On the surface of the earth, not exceeding depths greater than 300 ft, there exists a slight variation in temperature due to solar heat, cooling effect of ground waters and adjacent bodies of water, forests, vegetation, rain, snow, etc. Since these effects on drilling and production of crude oil are of minor importance, discussion of them will not be included in this paper.

Table 1. Subsurface Temperature of Oil Fields in Texas and Louisiana.

Division and Field	Producing Formation	Sub-Sea Depth	Temp. (°F)	Geothermal* Gradient (Feet per °F Increase)	Type of Structure
East Texas					
East Texas	Woodbine	3300	146	50.00	Stratigraphic Trap
Navarro Crossing	Woodbine	5545	184	53.31	P. T. Salt Dome
Oakwood	Woodbine	5610	186	52.92	Anticline Faulted
Van	Woodbine	2425	136	43.30	Deep Seated Salt Dome Faulted
Talco	Paluxy	3785	147	56.49	Anticline Faulted
Willow Springs	Glenn Rose	6925	221	49.11	Anticline Faulted
Gulf Coast					
Amelia	Frio	6480	164	77.14	Deep Seated Dome Faulted
Anahuac	Frio	7050	178	71.93	Deep Seated Dome Faulted
Cedar Point	Frio	5585	172	60.70	Deep Seated Dome Faulted
Danbury	Frio	5500	178	56.12	Piercement Type Dome
Dickinson (8000')	Frio	8000	199	67.22	Deep Seated Dome Faulted
(9100')	Frio	9060	217	66.13	Deep Seated Dome Faulted
(Gillock)	Frio	8750	207	68.89	Deep Seated Dome Faulted
Friendswood	Frio	5800	164	69.04	Deep Seated Dome Faulted
Hastings	Frio	6000	170	66.66	Deep Seated Dome Faulted
Lovell Lake	Frio	7475	172	81.25	Deep Seated Dome Faulted
Pledger	Frio	6730	170	74.77	Deep Seated Dome Faulted
Roanoke, La.	Frio	8390	196	72.32	Deep Seated Dome Faulted
Sugarland	Frio	3600	156	47.36	Semi-Deep Seated P. T. Dome
Thompsons	Frio	5250	162	64.02	Deep Seated Dome Faulted
Withers (Magnet)	Frio	5350	152	74.30	Elongated Deep Seated Faulted Dome
N. Crowley, La.	Frio	8600	196	74.13	Deep Seated Dome Faulted
Vanderbilt	Frio	5530	166	64.30	Deep Seated Dome Faulted
Conroe	Cockfield	4900	172	53.26	Deep Seated Dome Faulted
Hardin	Cockfield	7610	196	65.60	Faulted Regional Uplift
Livingston	Cockfield	4115	158	52.75	Deep Seated Dome Faulted
Raccoon Bend	Cockfield	3850	156	50.65	Deep Seated Dome Faulted
Segno	Cockfield	5060	165	59.52	Deep Seated Dome Faulted
Tomball	Cockfield	5380	182	52.74	Deep Seated Dome Faulted
N. Cotton Lake	Marginulina	6145	156	80.85	Closure on Fault (Part of S. Cotton Lake Structure)
S. Cotton Lake	Marginulina	6320	156	83.15	Elongated Faulted Regional Anticline
Hastings	Marginulina	5700	162	69.51	Deep Seated Dome Faulted
Roanoke, La.	Marginulina	8630	201	71.32	Deep Seated Dome Faulted
N. Crowley, La.	Marginulina	7970	188	73.79	Deep Seated Dome Faulted
N. Crowley, La.	Miocene	7020	169	78.87	Deep Seated Dome Faulted
Thompsons	Miocene	3450	146	52.27	Deep Seated Dome
West Columbia	Miocene	2350	126	51.08	Piercement Type Dome
Goose Creek	Miocene	2580	115	73.71	Deep Seated Dome Faulted
Cameron Meadows	Miocene	3925	139	66.52	Piercement Type Salt Dome
Barbers Hill	Miocene	4500	136	80.35	Piercement Type Salt Dome
Darrow, La.	Fleming	5760	167	66.20	Piercement Type Salt Dome
Hull	Saline Bayou	4500	145	69.23	Piercement Type Dome
Katy	Saline Bayou	7000	170	77.77	Deep Seated Dome
Kittrell	Carrizo	1710	121	41.70	Deep Seated Dome Faulted
Lake Hermitage, La.	Miocene	3175	117	85.81	Piercement Type Salt Dome
Lake Washington, La.	Cap Rock	1125	104	46.87	Piercement Type Salt Dome
N. Crowley, La.	Discorbis	7945	186	74.95	Deep Seated Dome Faulted
Raccoon Bend	McElroy	3250	142	52.41	Deep Seated Dome Faulted
Roanoke, La.	Heterostegina	7790	187	72.80	Deep Seated Dome Faulted
Segno	Wilcox	7540	221	53.47	Deep Seated Dome Faulted
S. Liberty	Saline Bayou	4925	142	79.43	Piercement Type Salt Dome
Southwest Texas					
Flour Bluff	Frio	6650	185	63.33	Deep Seated Salt Dome Faulted
Greta	Frio	5750	177	59.27	Anticline
Heyser	Frio	5360	164	63.81	Sand Lenses on Anticline
Kelsey	Frio	4495	158	57.62	Anticline
Kelsey	Frio	5800	182	56.86	Anticline
Plymouth	Frio	5575	165	65.58	Monocline
Tom O'Connor	Frio	5800	177	59.79	Deep Seated Dome
Colorado	Cockfield	2330	145	35.84	Monocline—Lens
Dirks	Cockfield	3510	149	50.86	Faulted Dome Structure
Voss	Cockfield	3550	150	50.71	Faulted Nosing Structure
Government Wells	McElroy	1750	128	36.45	Faulted Monocline
Loma Novio	McElroy	1950	138	33.62	Monocline—Lens
Lopez	McElroy	1610	124	36.59	Monocline Faulted

*Based on Assumed Average Sea-level Temperature of Texas and Louisiana of 80 °F.

Table 1. Subsurface Temperature of Oil Fields in Texas and Louisiana.—(*Continued*)

Division and Field	Producing Formation	Sub-Sea Depth	Temp. (°F)	Geothermal* Gradient (Feet per °F Increase)	Type of Structure
Southwest Texas—(Continued)					
Seven Sisters	McElroy	1900	132	36.53	Monoceine Faulted
Greta	Heterostegina	4150	143	65.87	Anticline
Hilbig	Edwards Lime	3175	116	88.19	Serpentine
Hilbig	Serpentine	2000	121	48.78	Serpentine
Kohler	Mirando	1825	137	32.01	Monocline
Lundell	McElroy	940	111	30.32	Monocline Faulted
N. Sweden	Pettus	4900	179	49.49	Faulted Anticline
O'Connor	Fleming	2950	121	71.95	Deep Seated Dome Faulted
Taft (4000')	Catahoula	3900	133	73.58	Deep Seated Dome Faulted
Taft (4900')	Heterostegina	4750	158	60.89	Deep Seated Dome Faulted
West Texas					
Hobbs	Permian Lime	500	98	27.77	Anticline
White and Baker	Permian Lime	5979	126	129.98	Anticline
Wink	Permian Lime	110	85	22.00	Anticline
North Texas					
Avoca	Palo Pinto Lim	1710		34.89	Anticline Faulted

With regard to temperature and structure, a regional temperature map of West Central Texas would show a comparatively high temperature gradient along the Balcones-Mexia-Lulling belt of faults.[10] Along this belt, temperatures increase 1 °F for each 43 feet of depth. West of this belt in the Central Mineral region, the increase is 1 °F for each 50 or 60 feet of depth. Still farther west and northwest, in the Permian Basin, the rocks are much cooler, the rate of increase being less than 1 °F for each 100 feet. Investigations by Heald[10] of four salt domes, three in the Gulf Coast and one in the "interior salt dome province," have definitely shown that there is a more rapid increase in temperature with depth as the highest point of the dome is approached. The observed increase along the Balcones fault zone is 1 °F for 50 feet of depth, and the highest temperature is definitely associated with the salt dome itself. The decrease in temperature gradient farther and farther away from the dome was unmistakable. To make the situation even more interesting, the work has shown that temperatures at depths as shallow as 200 or 300 ft were significant; this has not proved true in other parts of Texas.

The apparent concentration of heat near salt domes may be partially explained by the fact that salt is an excellent conductor of heat, and assuming that the salt plug extends to depths in excess of 20,000 feet, the high temperature existing at this depth would be more readily transmitted through the salt mass than through adjacent sedimentary formations.

Unfortunately, data on the actual temperature of a buried salt mass are not available. However, examination of Figs. 11 and 12[11] indicates that the circulation of ground waters in contact with the salt mass accounts for the decrease in temperature gradient along the flank and at a distance from the salt mass. These temperature gradient lines have a close similarity to the dip of the surrounding formations that have been uplifted by the intrusion of the salt mass.

(2) Table of Maximum Bottom-hole Temperature Recorded in Texas and Louisiana Oil Fields

A recent survey of maximum temperature measurements made opposite the producing formation in 75 Texas and Louisiana oil fields is given in Table 1, listing the producing formation, the sub-sea depth at which they are encountered, the average temperature, the geothermal gradient and the type of structure. The figures in the column "Geothermal Gradient" were arrived at by assuming the average sea-level temperature in Texas to be 80 °F, and simply dividing the sub-sea depth by the average temperature less 80 °F. This represents the depth in feet for an increase in temperature of 1 °F, and can be used as an arbitrary figure in a comparison of the bottom-hole temperature with the type of geologic structure.

Acknowledgment

The author wishes to extend his appreciation and thanks to Milton Mortimer Cooke, Petroleum Engineer for the writer, for his patient and valuable assistance in assembling and compiling data from many sources, and for many suggestions which were ultimately embodied in this paper.

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The Role of Temperature Control and Measurements in the Welding of Oil-well Casing

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Introduction

What Oil-well Casing Is

When a hole is drilled in the surface of the earth to an oil-producing formation it is necessary to line this hole with some material that will resist the caving of the walls and the entrance of water from upper water-bearing formations and that will also prevent dissipation of the oil and gas into upper permeable formations. The material now universally used for this purpose is steel pipe, usually known as casing.

Its Two Methods of Application

The practice, until quite recently, has been to use thread and coupled joints. Threads are cut externally on each end of the joints of casing, and the joints are then held together by internally threaded couplings. A new practice is becoming increasingly prevalent, namely, that of welding the joints together.

The Basis for the Successful Use of Welding

A satisfactory weld is one that has adequate strength and ductility and is free from quench cracks. To obtain such a weld under the conditions that must be met in the welding of casing necessitates the employment of a procedure that is exactly suitable. It has been found that the knowledge and execution of correct procedures are dependent on the ability of the operator to predict, measure and control the changing temperature in a cooling weld.

I. Changes in Steel Due to Temperature

When the temperature of a piece of steel rises from atmospheric to the melting point, then cools to atmospheric temperature once more, physical and metallurgical changes take place, and there are factors which cause these changes to vary.

Physical Changes

A. Changes in Crystalline Structure. The usual crystalline structure of casing steel at atmospheric temperatures is the body-centered cubic. If the temperature of this type of steel is increased from atmospheric it will eventually reach a temperature such that any further increase will cause such a change in the crystal potential as to demand a rearrangement of atoms in the crystals. This rearrangement will still leave the crystals in the cubic system, but it will now be what is known as a face-centered cubic crystal. The temperature at which this change takes place is usually between 1300 and 1700 °F.

B. Consequent Volume Changes. The face-centered cubic crystals are more economical in the space which they occupy; therefore, if the volume of a piece of steel is measured during an increase in temperature, it will be found that this volume increases in a fairly straight-line relation with the temperature to the point where this change in crystalline form takes place. Then the volume ceases to increase with the temperature and, in fact, decreases while the temperature is still increasing. This transformation from body-centered to face-centered crystals is not instantaneous, but takes place over a relatively short time. During this short time the volume in the piece of steel decreases. However, as soon as the transformation has taken place and the steel is all made up of face-centered cubic crystals, this decrease in volume ceases and the volume again increases as the temperature increases.

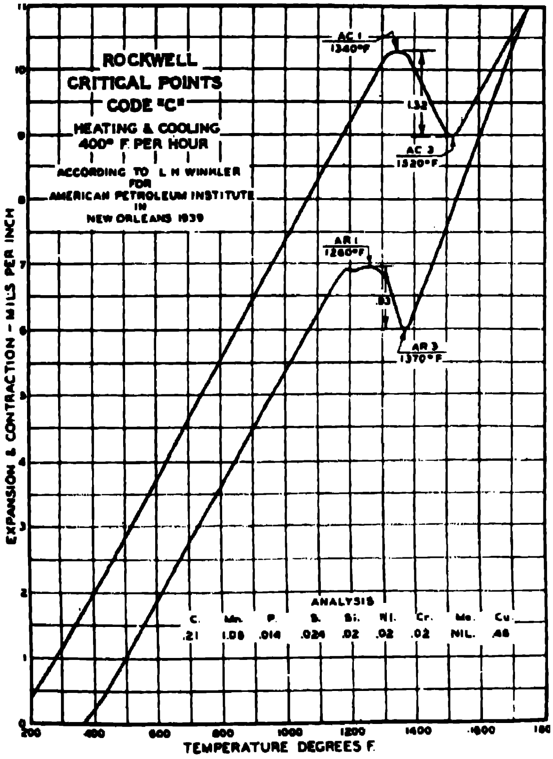

Fig 1.

The volume and temperature changes may be measured by instruments known as dilatometers. In Fig. 1 will be seen a typical dilatometer curve. The two points of this curve at which volume reversals occur during the increase in temperature are known as the critical points on heating, the lower being known as the Ac_1 point and the higher as the Ac_3 point. The time or temperature existing between the Ac_1 and Ac_3 points is usually referred to as the critical range on heating.

In Figs. 2 to 7 will be seen additional curves of the same sort as presented by L. H. Winkler, of Bethlehem Steel Company, to the American Petroleum Institute at New Orleans, 1939.

C. The Change in Magnetic Permeability. In addition to the changes in volume and crystalline structure, there are a number of other changes which take place when the steel passes through the critical range. However, it is desired to consider only those which bear on the practical problem under consideration; therefore, only the change in magnetic permeability will be considered other than those which have already been discussed. As the heating steel enters the critical range, the magnetic permeability decreases rapidly, and by the time it has passed through the Ac_3 point, leaving the critical range, the magnetic permeability has almost completely disappeared.

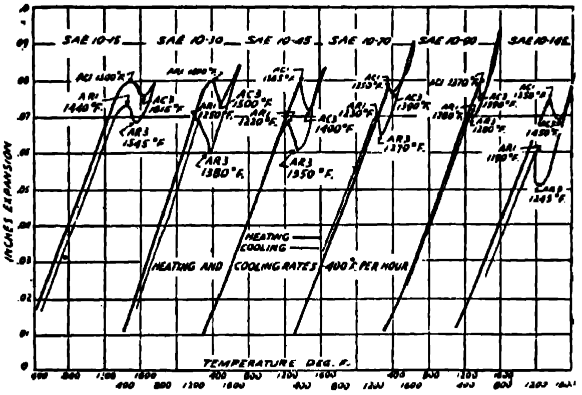

Fig. 2.

Thermal critical curves showing influence of variation in carbon content.

D. The Physical Changes on Cooling. If this piece of steel now is allowed to cool the changes roughly reverse themselves. First, the change in crystalline structure from the face-centered back to the body-centered cubic takes place; but there is a lag in the point at which it occurs as compared with the points at which it took place in heating. The reversal to the body-centered cubic always takes place at a lower temperature than the transformation from the body-centered to the face-centered occurred.

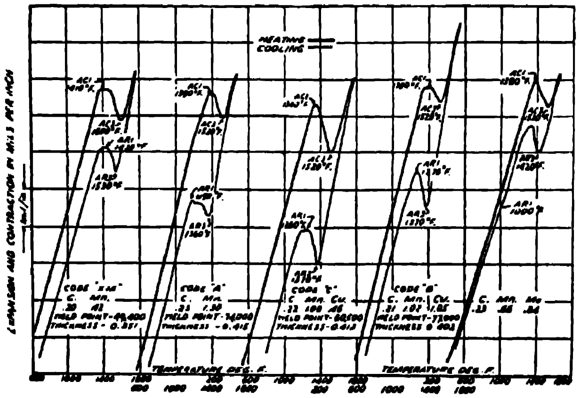

Fig. 3.

Effect on Rockwell critical points of addition of alloys to 0.20%-carbon steel.

As the crystalline structure changes, the volume necessarily changes with it. A slowly cooling piece of steel, on reaching the top of the critical range on cooling, ceases to shrink and begins to expand, and continues to expand until it has passed the critical range. The steel then ceases to expand and again begins to contract linearly with the decrease in temperature.

The temperature at which the magnetic permeability begins to return during the cooling of steel is essentially the same as that at which it was lost when the steel was heated. It may be a mistake to regard this as a point on the cooling curve, or, for that matter, on the heating curve. We have not discerned a point; on the other hand it is well-known that magnetic permeability is lost on heating over a range of temperatures, and returns on cooling over a similar range of temperatures. It has been found that, although the permeability begins to become measurable on cooling at essentially the same point at which it is lost to measurement on heating, this permeability increases as the steel continues to cool until the Ar_1 point is passed. So far as it was possible to determine, the end of the increase of the magnetic permeability on cooling was simultaneous with the passage of the Ar_1 point. The importance of this finding will be made clear farther on.

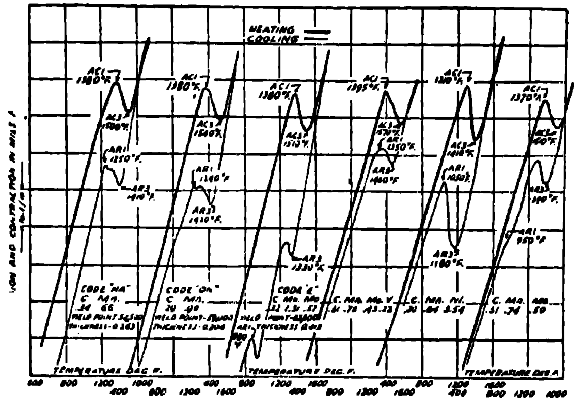

FIG. 4.

Effect on Rockwell critical points of addition of alloys to 0.30%-carbon steel.

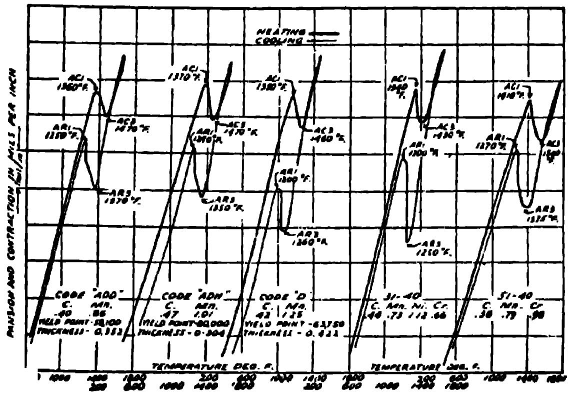

FIG. 5.

Effect on Rockwell critical points of addition of alloys to 0.40%-carbon steel.

Metallurgical Changes

Casing steel is made up of two constituents—pearlite and free ferrite. Pearlite is a mechanical mixture of cementite and ferrite. Cementite is iron carbide, and ferrite is iron in a body-centered crystal form.

When the temperature of this steel is increased through the critical range, these metallurgical and chemical distinctions are lost, and the steel passes into the form known metallurgically as austenite, in which the ferrite, the iron carbide, etc., have lost their identity and have become a relatively homogeneous mass. In the welding of casing this will, of course, happen at and in the near vicinity of the weld.

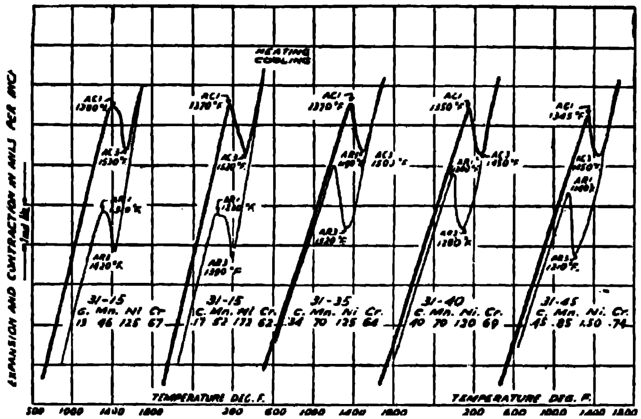

FIG. 6. Effect on Rockwell critical points of increasing the carbon content of an alloy steel.

If the metal is now allowed to cool slowly, the metallurgical transformation will reverse itself, the change from austenite to a mixture of pearlite and free ferrite taking place. If, however, the cooling is increased to an appreciably higher velocity, a different transformation will occur, resulting in a mixture of some pearlite and of some martensite.

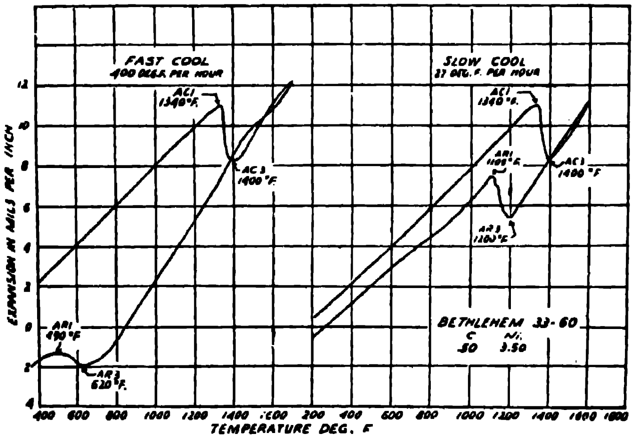

FIG. 7. Thermal critical curves showing effect of variation in cooling rate on the "AR" range.

It is not within the scope of this paper to discuss the metallurgical mechanism involved. It is sufficient to point out that the transformation product known as martensite is a very hard and strong material with little ductility. It is therefore highly undesirable in a weld.

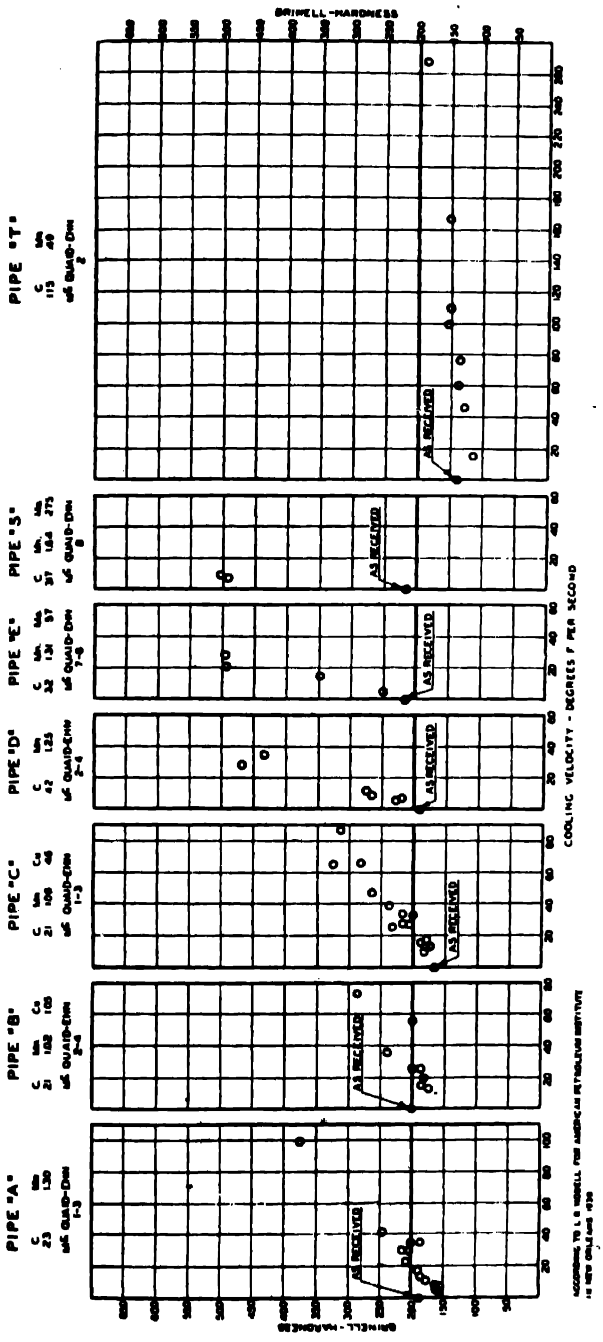

FIG. 8. Hardness vs. cooling velocity in typical casing steels.

II. Factors Varying the Changes

In a weld that has been skillfully applied (it being understood that in this case "skillfully" refers to the manual dexterity of the welder) the most convenient measure of the reliability of the weld is its final hardness. The American Welding Society sets as 200 Brinell the maximum hardness which is permissible in good practice in a weld that is not to be preheated, stress-relieved or annealed. In the practice of welding casing we accept this as a limit upon which to design our welding procedures.

The final hardness of a weld is a measure of the transformation products composing it. If the products are pearlite and ferrite, the hardness will not be great. As increasing proportions of the pearlite and ferrite are changed to martensite, the hardness of the weld increases. It has already been pointed out that the transformation products vary with the cooling velocity to and through the critical range. These products also vary with the chemical composition of the steel. Figs. 8 and 9 represent the results of an experimental program to determine this relationship. The measurement of the cooling velocity in each of the cases shown here was made at 1300 °F. Velocities resulting in a hardness of 200 Brinell or less are regarded as acceptable. Examination of these figures shows what, if any, limiting velocity exists for each steel.

It is apparent that the cooling velocity of the weld has been arbitrarily measured at 1300 °F, this being regarded as immediately above the critical range of most of our casing steels. It must be further pointed out, however, that the position of the critical range on cooling is dependent on the cooling velocity. The higher the cooling velocity, the more the temperature at which the critical range occurs will be depressed.

Since in applying casing it is necessary for a prompt fulfilment of the job to lower the pipe as soon as possible after completion of the weld, it is of the utmost importance that the time at which the critical range has been completely passed be accurately known. Lowering the hot weld into the drilling fluid before the temperature has passed the Ar_1 point on cooling greatly increases its cooling velocity above the critical point, and, as has already been stated and illustrated in Figs. 8 and 9, the result will be a greatly hardened weld.

III. Temperature Control in a Cooling Weld

The problem, then, of setting up a procedure for the successful welding of casing may be seen to consist of: (1) ability to anticipate and control the temperature of any point in the weld at any time after its completion; this, of course, implies an ability to deduce the cooling velocity of any point in the weld at any time after its completion; (2) ability to anticipate and know when the Ar_1 point actually has been passed. The attack on the problem has been threefold. It may be summarized as (1) analytical, (2) experimental and (3) instrumental.

Analytical

W. A. Bruce has developed an equation describing the cooling of a circumferential weld, which has been given previously.* The fundamental heat equation is

$$k\nabla^2\theta = \frac{d\theta}{dt} + \lambda\theta$$

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* American Physical Society, Washington, December 1938. Published in August issue of the *Journal of Applied Physics*, 10, 578-585 (1939).

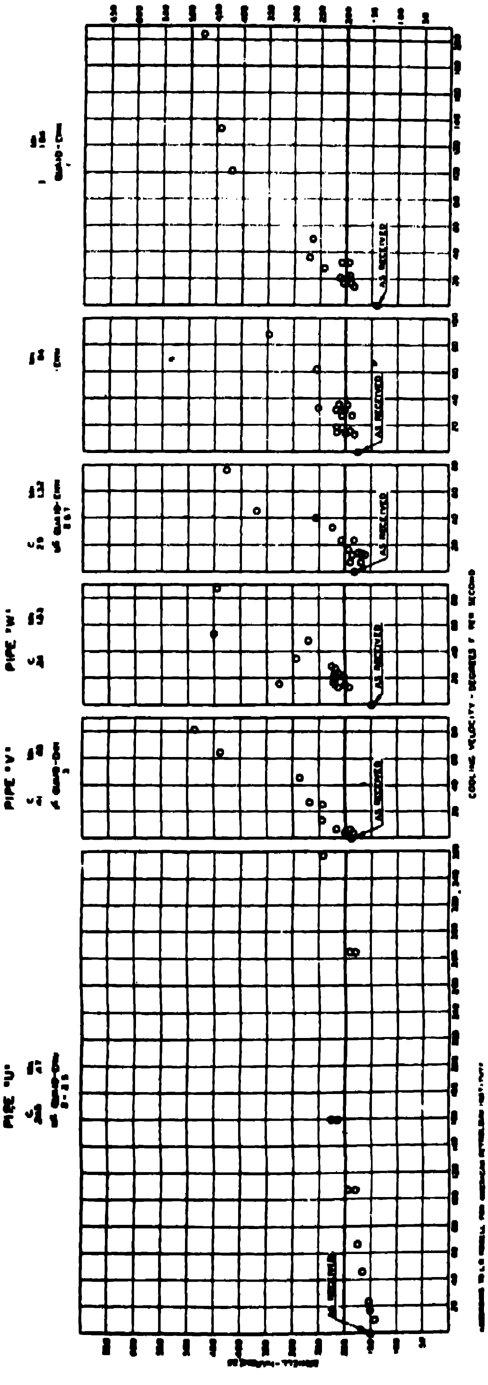

PIPE "U"
PIPE "V"
PIPE "W"
AS RECEIVED
AS RECEIVED
AS RECEIVED
AS RECEIVED
AS RECEIVED
AS RECEIVED
COOLING VELOCITY - DEGREES F PER SECOND

FIG.

where k=diffusivity,
θ=temperature,
λ=a radiation constant.

W. A. Bruce has shown that the temperature produced by a number of welders completing a weld on thin casing is given by

$$\theta = \sum_{n=-\infty}^{n=+\infty} \frac{q}{4\pi Kbv} \int_{nw}^{(n+1)w} \frac{1}{\left(\frac{x'}{v}+T\right)} . e^{-\lambda\left(\frac{x'}{v}+T\right)} . e^{-\frac{(x-x'-nw)^2+y^2}{4k\left(\frac{x'}{v}+T\right)}} . dx'$$

where w=separation of the welders,
v=velocity,
T=time after welders break arc,
$q'=\dfrac{q}{4\pi Kb}$,
q=calories per second,
K=conductivity,
b=wall thickness of the casing,
x=circumferential coördinate,
y=vertical coordinate.

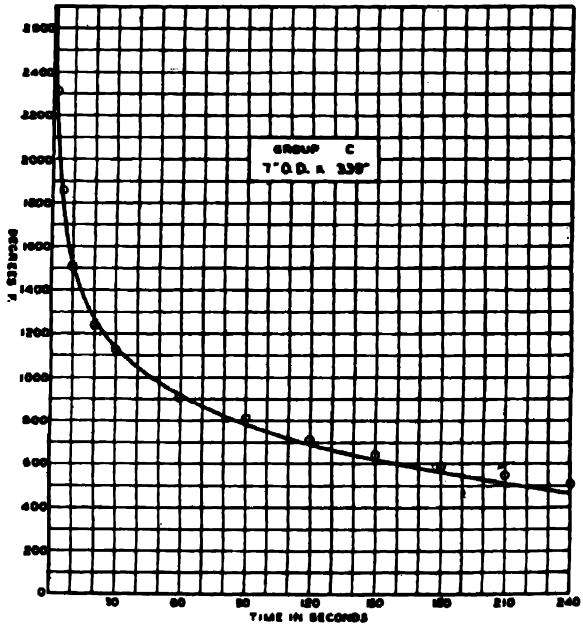


FIG. 10.

Fig. 10 is one of thirteen similar figures from an experimental program carried on by Bruce to determine the temperatures of the cooling weld in casing, as compared with the temperatures arrived at by means of his equation. The smooth curve represents the equation and the circles, the experimental points (see

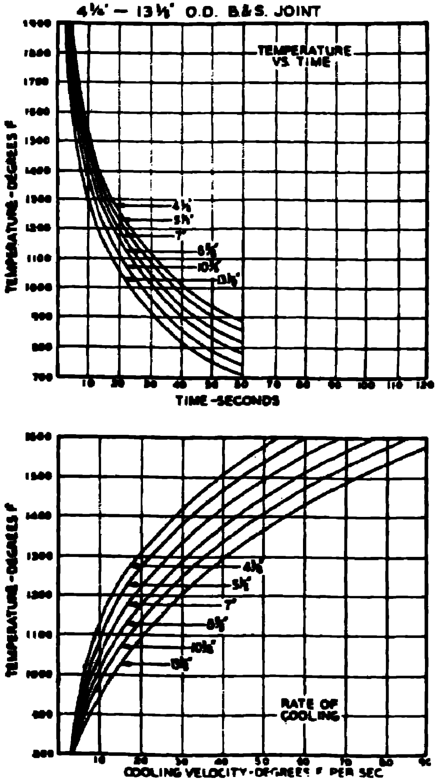
Table 1. Values of Experimental Data Averaged and Recorded by Groups.

Group	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Individual Test Nos.	2,3	5,7	6,8,9	11,12 13,14	15,16 17,18	19	20,21 22	27	29,30	31,32	33	61,62	72,73 74	75,76 77	80
Outside Diameter	$8\frac{5}{8}''$	7″	7″	7″	7″	7″	7″	7″	7″	7″	7″	$10\frac{3}{4}''$	$5\frac{1}{2}''$ B&S	$5\frac{1}{2}''$ B&S	$5\frac{1}{2}''$
Wall Thickness	.372″	.372″	.339″	.310″	.290″	.407″	.421″	.292″	.309″	.339″	.374″	.415″			.231″
No. of Welders	3	3	3	3	3	3	2	3	3	3	3	3	2	2	2
No. of Beads	3	3	3	3	3	3	3	2	2	2	2	4	2	2	2
Rod	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{1}{4}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$	$\frac{3}{16}''$
Ammeter Reading	153	140	151	156	153	210	160	140	154	154	162	225	219	228	180
Calories/Sec. per Welder			690	695			770	670					966	1020	
Time of 1st Bead, Sec.	69	62	72	73	51	185	102	64	74	81	85	67	35	37	36
Time of 1st Interval, Sec.	66	75	65	41	35	53	30	95	53	80	37	44	45	35	34
Time of 2nd Bead, Sec.	132	97	96	87	72	113	165	62	79	84	86	95	43	47	50
Time of 2nd Interval, Sec.	120	95	70	81	93		52					48			
Time of 3rd Bead, Sec.	106	69	57	53	51		128					92	Bell Thickness .232″	.280″	
Time of 3rd Interval, Sec.												38	Spigot Thickness .261″	.322″	
Time of 4th Bead, Sec.												91			
Temperature in Degrees F. vs. Time after Welders Break Arc — Time Sec.															
2	2700	1970	2310	2620	2600	2700	2700		2700	2400	2400	2500	2700	2700	2700
5	1840	1610	1860	2170	2030	2300	1970		2180	1870	1910	1790	1820	1820	2300
10	1430	1280	1510	1680	1560	1810	1440	1730	1780	1460	1500	1390	1390	1340	1840
20	1160	1120	1240	1310	1270	1440	1170	1310	1320	1200	1230	1180	1150	1070	1370
30	1040	1020	1130	1180	1150	1300	1070	1150	1170	1080	1110	1080	980	910	1220
60	840	830	910	980	930	1050	870	880	920	870	880	880	720	660	890
90	710	710	810	840	780	870	760	750	770	770	730	780	610	580	720
120	640	660	710	720	690	760	680	660	670	670	660	690	550	520	600
160	790	590	640	650	630	730	630	590	590			640	500	480	550
180	550	540	590	590	580		590	540	530			600	480	450	490
210	520	510	550				570		500				440	440	460
240	490	480	510				500						420	410	420
300		440											390	390	380

Table 1). From a practical point of view it is very evident that there is a close agreement between the analytical and experimental results obtained. Particular attention is called to the fact that there is no apparent temperature anomaly in this curve which would mark the passage of the Ar_1 point. This is due to the fact that the cooling of the weld in casing is maintained at an apparently even rate by reason of the very considerable difference existing between the temperature of the point under consideration and the temperatures at other points in the circumferential weld. If only a small portion of this pipe were taken, a temperature anomaly would appear in the cooling curve, but this anomaly is covered up in the cooling of the entire joint of pipe.

It has been found practicable to make use of this method of calculating and predicting the temperatures of a weld under any given set of welding conditions.

Since this equation has been successful in giving a practically acceptable representation of the temperature behavior in steel on cooling, it is apparent that the cooling velocity at any time may be obtained by differentiating the equation for the temperature existing at that time. Figs. 11 to 14 illustrate predictions resulting



Variation O.D. Thickness=0.330 in, amps, 2 welders, 2 beads, 4[illegible] conds between beads.

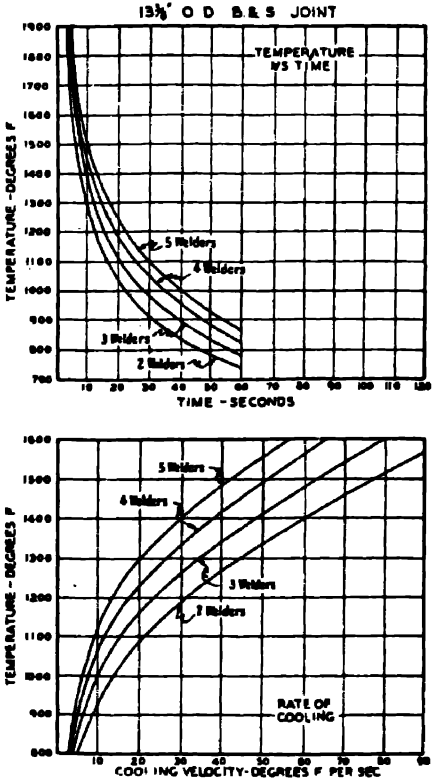


FIG. 2. Variatioı welders. Thickess=0.330 in, mı 2 beads 5 seconds bet ea

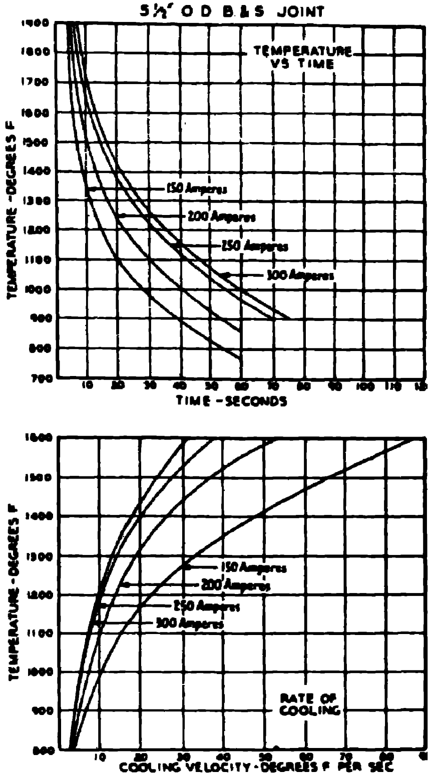


FIG. 13. Variation in amperes. Thickness=0.250 in, 2 welders, 2 beads, seconds between beads.

from computations of the temperature and cooling velocity in a weld and, therefore, by implication the planning of the proper procedure for a satisfactory weld.

It is seen, then, that the first problems in connection with establishing a proper welding procedure, namely, ability to predict and control temperatures, has been met both analytically and experimentally. The second problem, namely, the ability to predict and to know when the *Ar*₁ point has been passed, has been attacked both experimentally and instrumentally. In Fig. 15 are results of experimental work done on eight different casing steels for the purpose of determining at what actual temperature the *Ar*₁ point was passed under a range of cooling velocities.

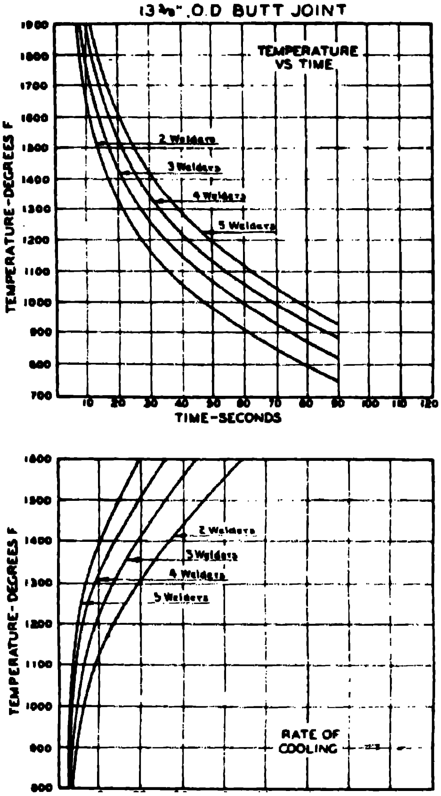


Fig. 14.

Variation in welders. Thickness=0.330 in, 200 amps, 2 beads, 45 seconds between beads.

The test procedure was as follows: A thin bar $\frac{1}{8}$ in square and 1 ft long was cut from a piece of casing to be tested. A furnace, consisting of a coil of Nichrome wire, was wound over mica insulation along the length of the bar. This furnace could heat the bar to 1800 °F. One end of the bar was fixed, and the other was connected to a spindle and mirror combination. As the bar expanded or contracted the mirror rotated, and a light shining on the mirror traced out a spot along a calibrated screen. With the aid of air, CO_2, and water, the bar was cooled at various rates, and the critical points marked for each of these rates of cooling. At the same time that this observation was made on the volumetric change, an observation was also made on the magnetic permeability. Fig. 19 indicates the apparatus used. As a result of this experimental program it was learned that,

when considering any given sample of steel taken from casing, reproducible results are obtained with good accuracy. It was found, however, that there would be some variation in the results obtained from two specimens taken from the same joint of pipe. This is due to the fact that commercial casing steel varies chemically to some extent from one point to another. It is felt, then, that the results of the experimental attack on this problem are not conclusive. It was originally hoped that it would be possible to determine experimentally the *Ar_1* point for a sufficient variety of casing steels so that the operator would need only to refer to a table. This, however, not being possible for the reason just stated, namely, that the commercial casing steel varies from point to point in chemistry and consequently in the position of the *Ar_1* point in the cooling curve, the problem has been attacked instrumentally.

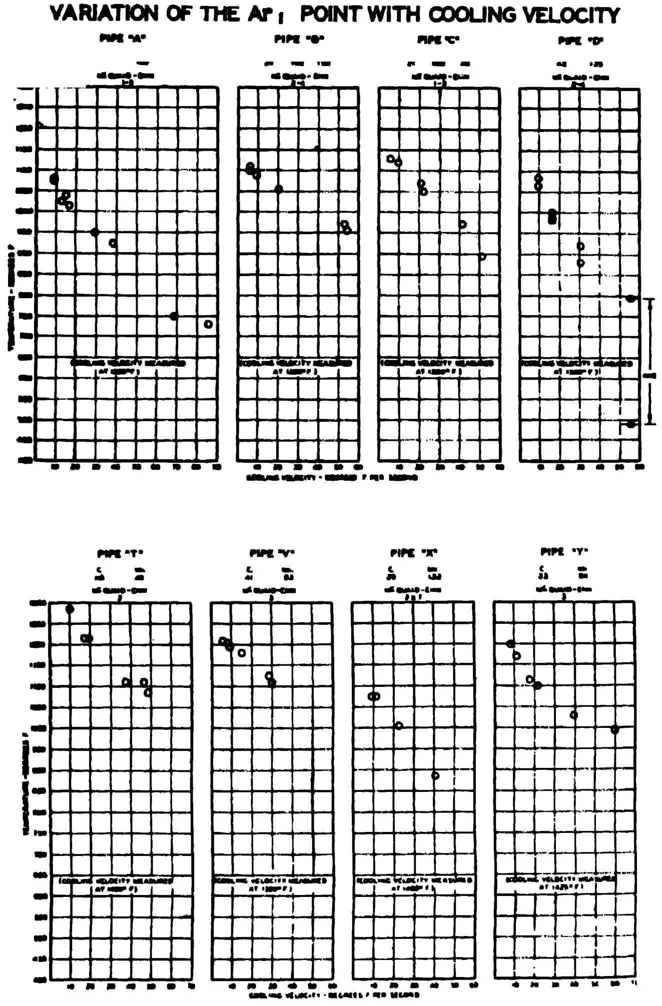


Fig. 15.

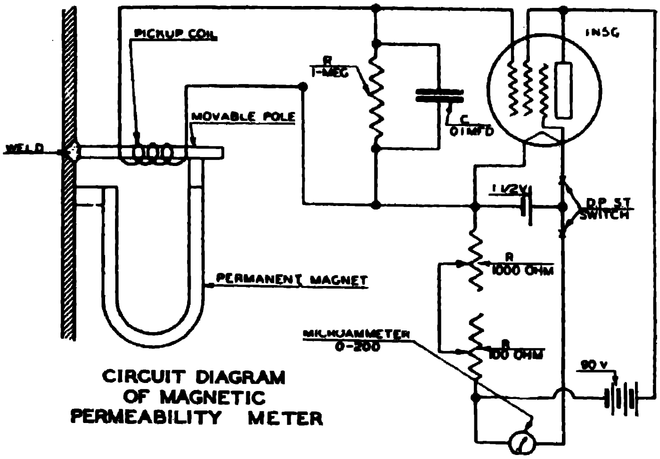


FIG. 16.

It is at this point that use is made of the knowledge that has been gained of the physical changes that take place simultaneously with the metallurgical changes when the steel cools through the critical range. The objective, as has already been stated, is to obtain a weld that has not been hardened by rapid cooling above and through the critical range. This objective is attained by setting up a welding procedure which will allow the steel to cool at sufficiently low velocity that the transformation products on cooling will be ferrite and pearlite, and not martensite.

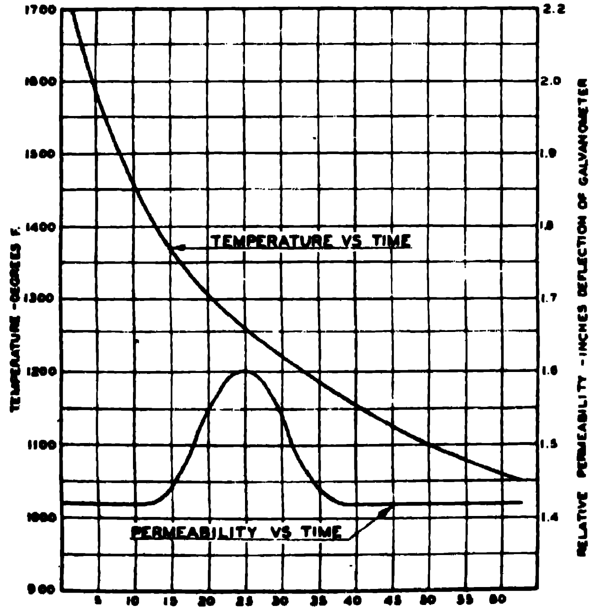


FIG. 17.

Since, however, it is important for practical reasons to shorten as much as is feasible the delay in lowering the casing after the completion of the weld, it is necessary to know, not only the proper cooling velocity (the velocity being measured at 1300 °F), but also the time or temperature when the cooling velocity no longer has any influence on the transformation products. When such a temperature has been reached, the casing may be lowered into the drilling fluid without affecting the weld. Since the temperature desired is the temperature at the Ar_1 point, the problem of instrumentation is to record accurately by some simultaneous signal the passing of the Ar_1 point. It has been pointed out that, in cooling steel, the magnetic effect reaches a maximum when the cooling temperature passes the Ar_1 point.

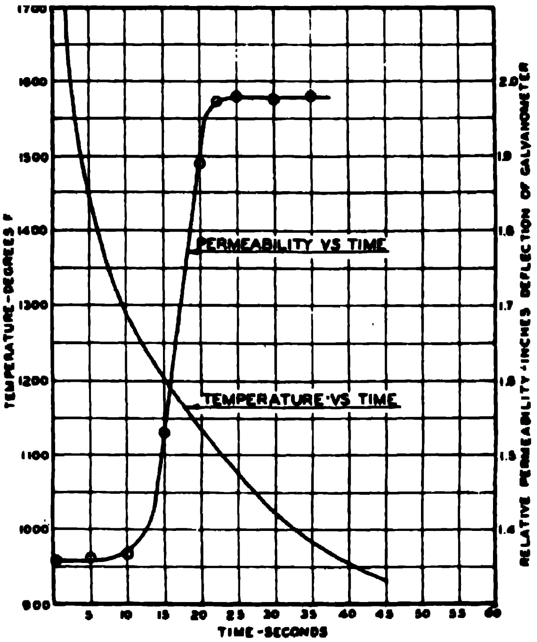


Fig. 18.

Obviously, then, an instrument which will measure the changing magnetic permeability in cooling steel will indicate, when it records the permeability at a maximum value, that the Ar_1 point has been passed and that, therefore, the weld may be lowered into the drilling fluid without damaging it by the formation of martensite.

Any of a large number of arrangements would give such a record. One such is shown in Fig. 17. In this figure will be seen what amounts to a magnet, which is applied across the weld and arrangements made so that changes in the magnetic permeability, when they occur, will be picked up, amplified, and recorded on a meter. In this design, D. C. current is used and a D. C. amplifier, the current being supplied from a battery. If readings are made on the meter simultaneously with the temperature decline, a record similar to that in Fig. 18 will be obtained, which shows that with this instrument there is an increase in the dial reading to a maximum and then a falling away to zero again. When the hand on the instrument has fallen back to the zero point, the Ar_1 point in cooling has just been passed.

In Fig. 18 it will be seen that the Ar_1 point has been passed at approximately 1165°. It would be possible to set up a device to measure this, using A. C., in which case a record of the instrument readings against temperature would be similar to those in Fig. 19. It would be possible to use an oscilloscope and, in fact, this has been used for this purpose. Further, there is probably a large number of other devices which may be used to measure the growing magnetic permeability in the cooling weld. When this permeability has reached its peak, the Ar_1 point has been passed and the hot weld may be lowered into the water without danger.

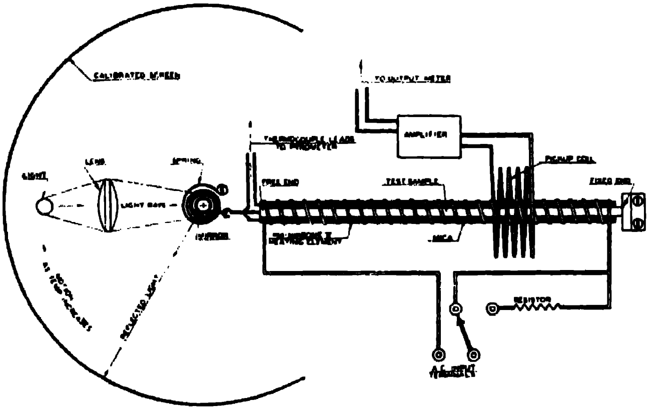


FIG. 19.

Summary

It has been demonstrated that the problems of temperature prediction, recording and control must be satisfactorily solved to make possible efficient welding of oil-well casing. Temperature prediction is done by means of mathematical analysis. The control of the temperature is obtained by reasoning from the predictions made as a result of the mathematical analysis. In the practical application of these methods to the running of oil-well casing, the planning of the welding procedure is made in this manner. This leaves the problem of determining accurately the passing of the Ar_1 point as the hot weld cools. The approximate position of the Ar_1 point, as it varies with cooling velocities, has been determined experimentally; but because of the varying chemistry of the commercial steels, this experimental method has not been found suitable for more than a rough prediction, and it has been supplemented by instrumental means of determining the actual passing of this critical point. The basis of the instrumentation is the determination of another physical property, namely, the growth of magnetic permeability, which reaches a peak at the same time that the Ar_1 point is passed.

Some Practical Considerations on Temperature Control

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In the early days of the oil industry, when petroleum products were processed by batch operation, the control of temperature was of minor importance. In batch distillation, for instance, where a shell still was charged with oil and the various products merely boiled off, fluctuation of temperature in the firebox was of no great concern, as it had little immediate effect on the temperature of the mass of oil under treatment, because of its large heat capacity. Later, however, when continuous processing superseded batch operation, the problem of temperature control became one of major importance, since it involved the matching of rates rather than quantities and any momentary change in the relationship of the rates resulted in improper processing.

Continuous processing forced the development, first, of accurate and reliable indicating and recording instruments and, later, automatic or "self-controlling" devices which bridged the gap between changes in a condition and the control of that condition. Distillation in a tubular heater, as we know it today, requires the maintenance of an accurate relation between the rate of firing and the rate of flow of oil through the pipe coil for successful fractionation. In cracking processes close control of temperature and flow is even more important, since it determines not only the quality of the product but the ability to run continuously.

The first attempts at automatic control of pipe-still and cracking-oil temperatures were crude in the light of present knowledge. These consisted for the most part of "on and off" controllers operating within 10° or 15 °F to cut or add fuel to the burners, or of mechanisms which opened or closed valves to change the flow of oil through the coil, depending only on whether the temperature was above or below the desired point. Their use resulted in a cyclic change of the temperature between wide limits, above and below the desired level, which served only to keep the system in a constant state of unbalance. Such control was useless and discouraging to the extent that some came to believe that automatic temperature control of stills was an impossibility.

It took a long time for instrument makers to understand the problems involved in process control and for the refiners, in turn, to appreciate the scope and limitations of instrumentation. Likewise, operators had to become familiar with automatic devices, which were regarded with great suspicion, perhaps justifiably so, in view of the dangerous nature of processing oil and the unsuitable character of the early mechanisms.

The automatic instrument has now become a familiar device in refinery processing as a result of the remarkable progress in this field in the past ten years. This progress has been largely brought about by better understanding of the factors involved in controlling refinery equipment, and the realization that disturbances must be analyzed and appropriately corrected. Hand control of temperature seems simple; but, when analyzed, it appears to be a complicated procedure involving judgment of the extent of departure, the rapidity of the change and the quantitative effect of corrections applied. The realization of the need of corresponding characteristics in control instruments has laid the foundation for present performance.

There exists a great similarity in all automatic control, whether directed toward purely mechanical motions, or toward complicated systems in which the effect of firing is eventually felt on a flowing stream of oil in a secondary system. The basic factors and their relationship can be expressed, in a general way, in the equation for the damped pendulum:

$$K_1\alpha + K_2\frac{d\alpha}{dt} + K_3\frac{d^2\alpha}{dt^2}$$

where α is the angle of departure and K_1, K_2 and K_3 are constants.

The significance of this relationship appears when considering the control of mechanical systems where the inertia is great, or in the control of heating in systems of large heat capacity and lag. It means that not only the direction and departure of the temperature from a given level be taken into account but, likewise, the rate of departure and perhaps even the change of rate or acceleration as well. It also indicates that the correction should be made in proportion to the net effect of all these factors during a disturbance, and that if this can be done the condition will be restored to its original value without over-shooting or under-shooting.

Increasingly close control of conditions already has resulted in greatly improved refinery operation, not only because of its direct effect on processing but because of the increased knowledge of the nature of chemical changes taking place, which has been gained by observation under constant conditions. Likewise, the continued demand for better refinery products has stimulated development of instruments capable of ever closer control. We have gradually come to realize that the effect of temperature changes on reactions is far-reaching; whereas, for instance, in years past a 2° or 3° deviation in the cracking temperature was considered permissible, we now know that even this departure results in so great a change in the cracking effect as to warrant striving for control within a fraction of a degree! We appear to be on the threshold of a new area in instrumentation and control which, for the lack of a better term, might be described as one of "super-control."

A number of instruments embodying sound principles of operation are available today. They are capable of very close control if properly fitted into the scheme of processing, and it seems probable that the next decade will see processing carried out with no perceptible change in temperature or other major factors. Such a goal will undoubtedly make possible results of thermal treatment heretofore unknown.

To develop effective control beyond that of the present will require close coördination between the practical and theoretical aspects of control systems. As much stress will have to be laid on improvements in process design, installations, and means of safeguarding the accuracy of readings as in the improvement of the actual control mechanism itself.

Confusion sometimes exists concerning the scope and ability of an automatic temperature control system or, in fact, of any automatic control device to produce a given result. Although such systems may function perfectly, the process results obtained may be far from those desired. In order to put an automatic system to effective use, it must be considered an integral part of the processing scheme and, furthermore, it should not be called upon to annul the shortcomings of equipment. Process equipment should be designed with a view to stability of operation, so that the control system is called upon only to rectify certain momentary changes. Control systems should not necessarily be limited in scope, and should be capable of taking care of wide fluctuations when necessary; but they should tend to level off and balance conditions rather than be called upon to correct chronic "drifts" from desired levels.

Temperature-control devices are often operated under unwarranted handicaps. For instance, in a split-flow coil, where there are two streams of oil heated in a common firebox, it is evident that the measurement of the temperature at the outlet, which is the average of the temperatures of the two streams, is not directly indicative of the heat treatment to which the oil in each half has been subjected. Controllers can be made to keep a satisfactory temperature record; but in this case the overall result may not show much improvement in the process. This is particularly true in a cracking operation, where variations in the time element have a major influence on the extent of cracking.

One of the most striking examples of futile use of temperature control is illustrated by the operation of a cracking heater on which tests were made by the writer some years ago. The heater was of the conventional box type with a radiant section and convection section comprising about 10,000 linear feet of pipe, most of which was disposed in the back pass and heated by the convection gases. The temperature-control device appeared to maintain a reasonably good outlet temperature record by varying the fuel to the burners. The coil, however, coked up with great regularity after two or three days of operation when reasonable yields were attained. The solution to the mystery appeared in the rate of gas production from the unit, which fluctuated over a wide range regardless of the stability of the outlet temperature. Upon investigation, it was found that in order to maintain the temperature the variations in fuel, initiated by the controller, changed the fuel-air ratio in the fire-box to such an extent that the heating effect in the convection bank changed over a wide range. This caused the point at which the cracking began to move forward and backward in the coil. Sometimes the effective time element was longer and sometimes shorter for the constant outlet temperature. The crack—per pass—varied accordingly, and when too high it caused coking in the tubes. Obviously the controller mechanism, in this case, functioned correctly enough, but could not produce a useful result until the heater and firing systems were remodeled.

In coil cracking, temperature control has been applied generally to the outlet of the coil and has been very successful in the past. We now realize, however, that the cracking effect in a long coil is not directly proportional to the outlet temperature but to the temperature gradients all along the coil, and that the control of the outlet is only an approximation. The total cracking effect is obtained by subjecting the oil to heat over a wide range of temperature from the entrance to the outlet, and the magnitude of the crack-per-pass is determined by the time-temperature effect as a whole.

Obviously, control at any one point has shortcomings, and it seems probable that in the future we shall see control of temperature not only at the outlet but along the coil at a sufficient number of points to insure a definite and accurate cracking effect which, in turn, will permit making more definite products. Moreover, it seems probable that the control of a cracking coil may be accomplished by a more general type of controller which will measure the cracking effect as a whole and maintain this constant by resetting automatic controllers for temperature, flow and pressure.

Whatever direction the development takes, it has one objective—a more satisfactory overall result. Such a goal will have to be attained not only by improvement of individual controllers, but by their coördination in processing systems which tend, by design, to be stable and amenable to control.

The development of controller mechanisms has, in a way, over-shadowed development work in the thermocouple itself. Although considerable progress has been made in this field, such as improvement in metal compositions, wires, and construction of couples, there still remains considerable opportunity for improvement. Obviously, the function of the controller lies in decoding the stimulus produced by the thermal junctions, to note whether it is occurring rapidly or slowly, and to command an appropriate correction, taking into account the rate at which these corrections are taking effect. It cannot, however, distinguish between a true and a false reading, nor tell whether the thermocouple reflects accurately what is occurring in a reaction zone. The thermocouple must be relied upon to furnish a stimulus which bears a correct relation to the temperature to be controlled and must be in a position to receive changes promptly and, finally, maintain its calibration.

The thermo-well, which protects the couple, must necessarily be properly immersed in the stream and yet not impede the flow or become a carbon catcher. The shape and position with respect to the tube and fitting must receive careful consideration. In many cases it should be streamlined and be proportionate in size to the cross-section of the stream. The heat capacity of the well and fitting and the effect of radiation have an important bearing on the operation of the system as a whole; likewise the care it receives on shut-downs and the maintenance of electrical circuits during operation. All these factors combined with reliability and accuracy of the thermocouple, *per se*, are obviously of prime importance, for all the skill of designers of instruments and of processes can be rendered useless by apparently trivial occurrences, such as a partial short-circuit or a loose connection in the thermocouple circuit.

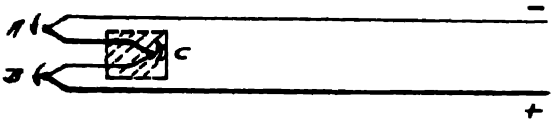

FIG. 1.

The thermocouple is generally employed at present simply to measure temperature in terms of the emf produced at the bi-metallic junction. It seems entirely possible that the future will see devices to amplify this current which will make changes in temperature more apparent which, in turn, will permit speedier and more accurate corrections. It is also possible that thermocouples themselves will be made to react not only as devices to measure true temperature but to produce a modified impulse by taking into account rate of change.

For instance, some experimental work has been done on multiple-junction couples, as illustrated in Fig. 1. As will be seen, the device consists of two "live" or uninsulated junctions, *A* and *B*, and one insulated junction, *C*, connected in series and immersed in the same temperature measurement zone. Arrows indicate the direction of rise of emf. At temperature equilibrium the emf from junction *A* is cancelled by that of *C*, for example, and the net emf of the series is equal to that of one junction, *B*, which may be called the measuring junction. During a change, however, junction *C* receives or loses heat at a lower rate than *A*, and the resulting temperature difference between them produces a differential emf of a sign and magnitude corresponding to the direction and rate of temperature change; to such extent the impulse from *B* is modified.

The utilization of such a device presents distinct possibilities, since it would tend to reduce the complication of the controller and consequently lead to less maintenance and opportunity for error. Certainly there appears to be a fruitful field for research in this direction.

Although it may seem unnecessary to bring out the necessity for proper maintenance in temperature controllers, so much grief has been experienced by the writer in the past through zealous but improper maintenance that it is perhaps worth while to touch upon this phase of operation. Controllers must not only be required to function properly, but they must constantly be watched to see that their functioning produces the desired result. This requires coördination between the process operators, and the instrument maintenance force. For instance, a good controller will often maintain a constant outlet temperature with a wide variation in fuel to the burner. This may be caused by improper control of flow, faulty pumps, plugged return lines, etc. The ability of the controller to maintain a good outlet record may constitute a victory for the controller, but does not insure good processing nor prevent warped tubes and high maintenance in the combustion chamber caused by too great a variation in fuel. Proper maintenance should take into account such unusual conditions, and the remedy should be sought by both the operators and the instrument men jointly for truly useful results.

The striving toward more accurate and stable processing conditions cannot be satisfied by mere perfection of any *one* mechanism, for it is obvious that control devices cannot be expected to overcome effects beyond their sphere of action. There will be, without doubt, great improvement in control devices in the future, but it should be borne in mind that the equipment of today is capable of far better performance than is generally obtained. As time goes on, improved knowledge of the scope and limitation of mechanisms will in itself constitute progress.

The foregoing has drawn attention very briefly to certain practical aspects of automatic control which, although obvious enough when viewed in detached form, are often hidden in the mass of plant equipment and the routine of operation. It is hoped that these few observations may be helpful in fostering improved results with existing equipment and point the way toward the coming era of real control accuracy.

The Significance of the Critical Temperature of Mixtures

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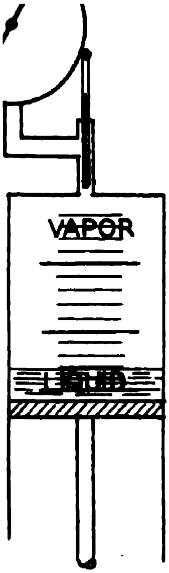
The object of this paper is not to present new results, but to call attention to a set of phenomena which appear to be unfamiliar to most physicists and chemists, which are not fully described in readily accessible publications, and which are of considerable importance to the petroleum industry.

The discussion will be confined to miscible liquids, that is, mixtures of substances for which only one liquid layer can be formed, such as mixtures of alcohol and water, or petroleum fractions. Mixtures such as oil and water, for which two liquid layers can be formed, are not considered here. The phenomena which can occur in the latter case are much more complex, and have been very little explored experimentally.

FIG. 1.

Schematic diagram of an apparatus for demonstrating the pressure, volume and temperature relations for pure substances and mixtures.



The Behavior of Pure Substances

It is convenient to begin by reviewing the well-known behavior of pure liquids and the vapors formed from them. If pure water, for example, is heated in an open vessel at one atmosphere pressure, it begins to boil at 100 °C and will be reduced completely to vapor at that temperature if the boiling is continued long enough. If the pressure is higher or lower, the boiling point will also be higher or lower.

In order to follow the volume occupied by the original mass of water, we may imagine an experiment conducted in a somewhat different way. Let the sample of water (for example, 1 gram) be confined in a tube with a perfectly fitting piston, with means for observing and controlling the temperature, and for observing the pressure on the piston and the position of the piston, which determines the volume occupied by the gram of water * (Fig. 1).

If we introduce pure water ahead of the piston, apply a high pressure, and gradually reduce it, the temperature being kept constant at (say) 100 °C, by appropriate introduction of heat, the volume of the gram of water will change very little until the pressure within the cylinder has been reduced to one atmosphere absolute. Then the pressure will remain constant as the piston is withdrawn until the volume has been increased to about 1670 cc. In this interval there will be a mixture of liquid and vapor within the chamber. Beyond a volume of 1670 cc the pressure will again fall off, the water being now in the form of superheated vapor. If the motion of the piston is reversed, the opposite changes will occur.

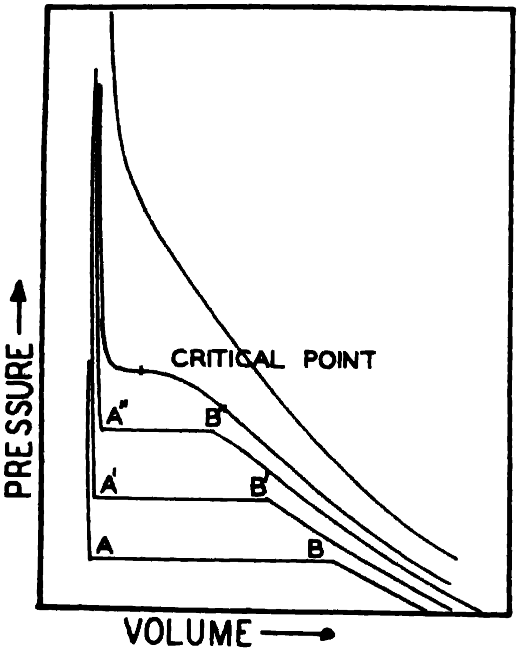


Fig. 2.

The pressure-volume relations for a pure substance at a series of constant temperatures. It is to be noted that the volume is independent of the pressure during condensation of the vapor (or vaporization of the liquid) and that the difference between the volume of the saturated liquid and vapor decreases with increasing temperature until it becomes zero at the critical point.

If the same procedure is followed at a higher temperature, a similar result will be observed, but the pressure at which a halt in the pressure change occurs (the vapor pressure) will be higher, and the volume when vaporization is complete will be smaller. In Fig. 2, in which volume is plotted against pressure for various temperatures, these points are brought out graphically.

As the temperature is further raised, the vapor pressure will be further increased, the volume of the liquid at the boiling point (points *A*, *A'*, *A''*. etc.) will increase and the volume of the saturated vapor (points *B*, *B'*, *B''*, etc.) will decrease. Finally a temperature will be reached at which the horizontal portion *AB* will decrease to zero. This is the critical temperature, and the pressure and volume at the (infinitesimal) horizontal portion are the critical pressure and volume. Above this critical temperature two layers cannot exist in the chamber, and no horizontal portion of the curve will be found.

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* This arrangement is actually used in some experimental work, the piston being generally a column of mercury, the pressure on which is measured to determine the pressure in the confined fluid. (There will be a small correction for the pressure exerted by the vapor of mercury.)

In Fig. 3 a vapor-pressure curve, relating the temperature to the pressure of the horizontal portion, is drawn. It ends at the critical point. Similar curves exist for all pure liquids, if they do not decompose below the critical temperature.

The critical temperature, pressure, and specific volume or density are constants characteristic of the substance. A knowledge of these constants is of value, not only in defining the limits within which liquid and vapor can coexist, but also in the study of the density changes of the substance, quite outside the region of boiling and condensation. For it has been shown that if we take two substances, each at an absolute temperature and an absolute pressure which is the same percentage of the critical temperature and pressure of the respective substances, then the densities of the two substances will be the same percentage of the critical density. This rule, which is known as the law of corresponding states, is valid only to a first approximation, the result being more correct for closely related substances. It is, however, of great value in correlating data on the density of gases, especially at high pressures; it is of much less value for liquids. The absolute temperature of a substance, divided by its critical temperature, is known as the reduced temperature, and similarly for the pressure and density.

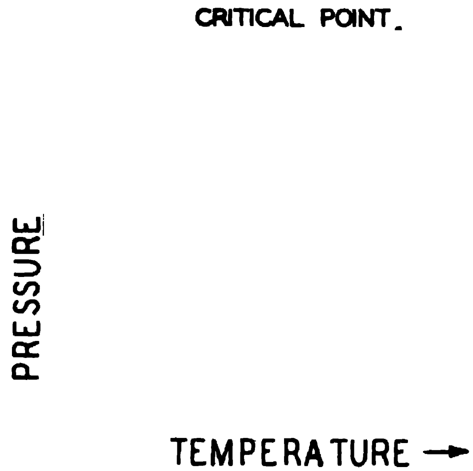

FIG. 3.

The relation between the vapor pressure and the temperature of a pure substance is represented by a curve. This curve ends at the critical point which is the highest temperature and pressure at which the liquid and vapor layers can coexist.

The Behavior of Mixtures

Now suppose that within the chamber of Fig. 1 is a mixture of substances which are miscible in all proportions. Unless the contrary is stated, the statements apply to any mixture of miscible liquids, no matter how complex. Assuming, as before, that a high pressure has been applied to the piston, the temperature being fixed at a suitable level, the tube will contain only liquid. As the pressure is reduced, a small increase in volume will at first be observed. At a certain pressure (the "boiling point" or "bubble point") a vapor layer will appear in the tube, and the increase in volume for a given reduction in pressure will be much greater.

The mixture will behave differently from the pure substance previously discussed, in that the pressure will not remain constant as the piston is further withdrawn, but will continue to fall as the liquid in the tube is vaporized. When all the liquid has just disapeared (the dew point), further increase in volume will cause a more rapid fall in pressure, as in the case of the pure substance. Reversing the motion of the piston will produce the opposite changes.*

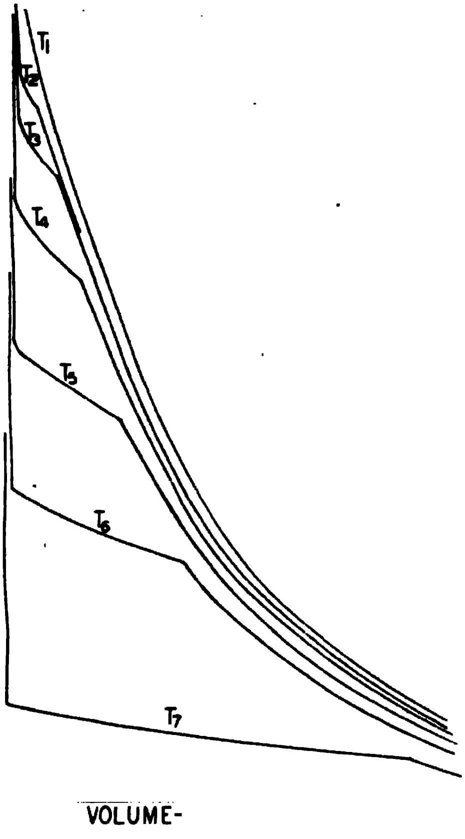

FIG. 4.

Relation between volume and pressure for a mixture at a series of constant temperatures. The pressure changes during vaporization (or condensation) of the mixture, which in this respect does not behave like a pure substance.

If the experiment is repeated with the same mixture at a higher temperature, similar results will be observed, but the boiling point and the dew point will be observed at higher pressures, and the difference between the corresponding densities will be smaller, the vapor density being greater and the liquid density less.

The relation between pressure, volume, and temperature for a mixture is illustrated in Fig. 4. It will be noted that the isotherms in the interval between the bubble point and the dew point are not horizontal, but that there are sharp breaks in the isotherms at these points.

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* In making experiments of this sort in mixtures, it is necessary to agitate the two layers before taking readings. Otherwise, equilibrium will not be reached at once, and the readings will change with time.

In place of the single vapor-pressure curve for a pure substance, mixtures have therefore two curves, the dew line and the boiling line, between which the pressures and temperatures for coexisting vapor and liquid layers for a particular mixture are contained. Each of these lines has the same general trend as the vapor-pressure line for a pure substance. This is illustrated in Fig. 5.

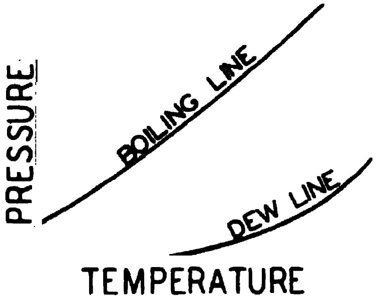

FIG. 5.

The pressure-temperature relations for a mixture in the region where vapor and liquid coexist are represented by an area bounded by two curves, the dew line and the boiling line, the former giving the pressure-temperature conditions where the mixture is completely vaporized, the latter where the mixture is completely condensed.

In considering the phenomena which occur as the temperature is raised further, it is convenient to distinguish between the effects which relate only to the volume of the whole system and those which relate to the amount of the two layers. If the experiments are conducted in a steel tube, so that the only information is that derived from the pressure-volume curves like those of Fig. 4, it will be found that at sufficiently high temperatures the dew line and boiling lines (as defined by the breaks in the isotherms) approach each other and merge into one continuous curve, the border curve for the mixture. An example of such a curve is shown in Fig. 6. Above the temperature represented by the maximum of the curve (point *E*) or above the pressure represented by point *D*, the given mixture will not exhibit any breaks in the isotherms, and hence no second layer is formed. But neither of these points is the same as the critical point for a pure substance. The point of maximum pressure is not the point of maximum temperature, and vice versa; whereas, for a

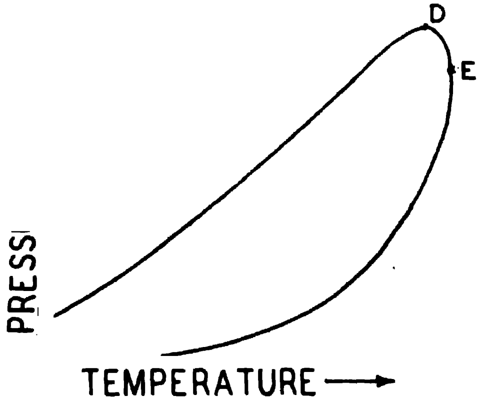

FIG. 6.

The border curve of a mixture. Within the area bounded by the curve the mixture is composed of a layer of liquid and of vapor. *D* is the highest pressure and *E* the highest temperature at which the two layers can coexist.

pure substance the critical point represents at once the highest temperature and the highest pressure at which two layers can coexist.

If the experiments are conducted in a glass tube, so that the behavior of the two layers can be observed, it will be found that various mixtures (even mixtures of the same components in different proportions) exhibit differences which are not reflected in the form of the border curve. The nature of these effects can be most clearly understood by representing on the pressure-temperature diagram the percentage (by weight, for example) of the substance which is in the form of liquid at any point.* The dew line will, of course, be a line representing zero per cent liquid, and the boiling line represents 100 per cent liquid. Between these lines other lines may be drawn, showing the pressure and temperature at which 10, 50, 90, or other percentages of the mixture will be liquid. If this is done, the results may assume any of the forms shown in Fig. 7.

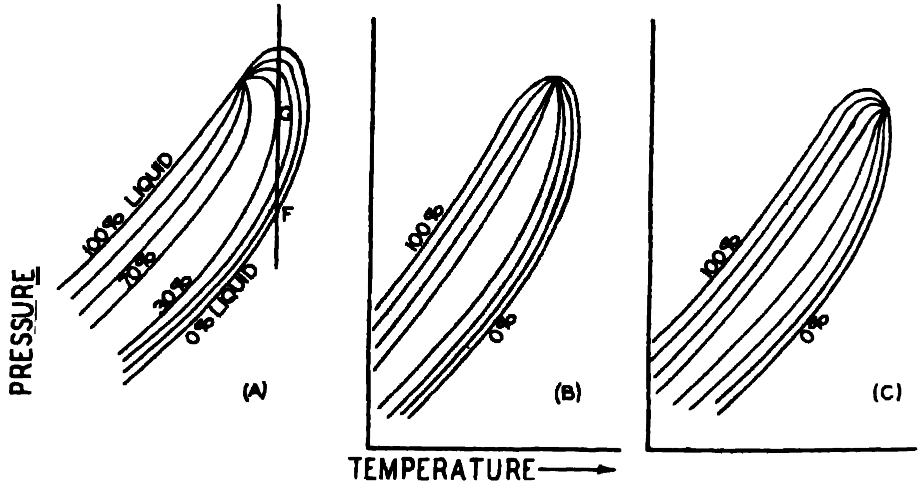

Fig. 7. Lines representing different percentages of the liquid in the vapor state all converge to a point on the border curve in the high-pressure region. At this point which is called the critical point of the mixture, the liquid and vapor layers have the same composition and the same properties and, therefore, cannot be distinguished from each other. The critical point may be located at any point along the rounded top of the border curve. Between the critical point and the highest temperature on the border curve the phenomenon of retrograde condensation occurs.

It will be noted that in all cases the curves for various percentages converge to a point on the border curve, but this point is not necessarily located at the top of the curve. It may be at any point along the rounded top of the border curve. It is not known how far from the top the point may lie; however, the rather limited number of experimental studies has not revealed any cases in which it lies below the point of maximum temperature.

The term "critical point" for a mixture is generally reserved for this point of convergence, although it does not possess all the properties of the critical point of a pure substance. This point is also called the plait point.

It will be noted that at temperatures higher than the critical temperature the behavior of a mixture with respect to compression is peculiar. Starting at the point *F* (Fig. 7a) the tube is filled with vapor. If the pressure is raised at constant temperature a liquid will appear in the bottom of the tube. This will increase up to a certain point, *G*, as the compression is continued. Beyond this point further compression causes the liquid to *disappear*. The reverse effect occurs when the pressure is lowered. This paradoxical phenomenon is generally called "retrograde condensation." It can occur with almost any mixture, between the maximum possible temperature and the critical temperature. Somewhat similar phenomena, of course, are found in the critical region when the pressure is kept constant and the temperature varied; but this case is more difficult to realize experimentally, whereas retrograde condensation has often been observed.*

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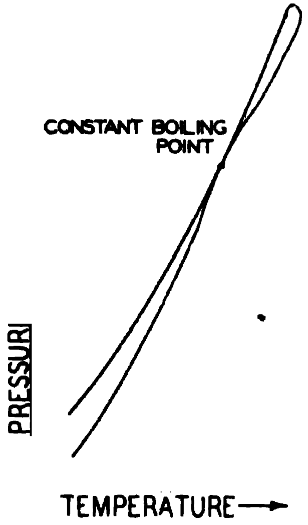
* In practice, the drawing of such curves implies a knowledge of the density of the layers at each point.

FIG. 8.

The border curve of a mixture which exhibits a constant boiling point. The dew line and boiling line are tangent to each other at the pressure and temperature of the constant boiling point.



The critical point defines the separation of the dew line from the boiling line, provided the definition of liquid and vapor which is most convenient be adopted. That definition is: If in a homogeneous substance a slight increase or decrease of pressure or temperature causes the formation of a small amount of another layer, then, if this new layer is lighter than the bulk of the mixture, it is a vapor, and the main bulk of the substance is a liquid; and vice versa if the new layer is heavier.

Composition Relationships

So far no mention has been made of the composition of the two layers. Actually, in every case save two, the two layers formed in the case of a mixture differ in composition from each other, and therefore from the composition of the whole material confined in the tube.

One case is that of the constant-boiling mixture. It may happen that for a given mixture there is a particular pressure for which the two layers have the same composition. It can be shown thermodynamically that in this case there will be no change in pressure during the course of the vaporization at the appropriate temperature; and correspondingly if vaporization is performed at this temperature there will be no change in pressure. Under these conditions the mixture behaves like a pure substance. But at any other pressure there will be some change in pressure or temperature during vaporization; naturally, at conditions close to those for constant boiling, the variation will be slight. Only certain mixtures exhibit this phenomenon. In the border curve for such a mixture the two sides touch at the constant-boiling point, as shown in Fig. 8.

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* If the critical point lay beyond the point of maximum temperature, the phenomena would be somewhat different. The effect has been called "retrograde condensation of the second kind," but it has never been observed.

The other case of similarity of liquid and vapor occurs for all mixtures at the critical point as defined above. At this point the density and composition of the two layers become identical, and this is the reason for applying the name to the point in question, especially since this identity of liquid and vapor produces the phenomena of opalescence which are observed at the critical point of pure substances.

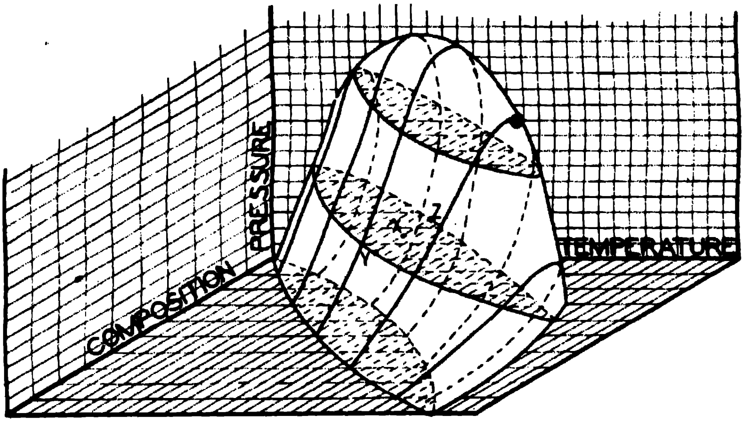

Fig. 9. The relations between the pressure, temperature and composition of a binary system are represented by a solid, and curves of intersection of a series of planes of constant pressure and constant composition are shown. A mixture represented by the point *X* exists as a layer of liquid and of vapor whose compositions are given by the points *Y* and *Z* on the surface of the solid.

Since the composition of the two layers is the same at the critical point, it follows thermodynamically that total vaporization or condensation will take place without change of temperature or pressure. It is easy to see, therefore, why the lines of constant percentage of liquid converge to this point, at which any percentage of liquid may be found.

Relation of Critical Temperature of Mixtures to that of Components

Generally speaking, there is no way of predicting the critical behavior of a mixture from that of its components. For a mixture with more than two components, there are no experimental data, and the number of binary mixtures examined is quite small. However, a consideration of binary mixtures sheds light on the conditions affecting the position of the critical points.

If we consider, not simply a mixture of (say) 50 weight per cent of one substance and 50 weight per cent of another, but all possible mixtures of these two substances, there will be for each mixture its own border curve (degenerated to a vapor-pressure curve for the pure components) each with its critical point. It is possible, then, to make a solid diagram having the coördinates, pressure, temperature, and composition embodying all the border curves. An example of such a diagram is given in Fig. 9. All two-layer mixtures are contained within the surface. Any section cut by a plane of constant composition represents a border curve for the corresponding mixture.

The shape of the surface shown in Fig. 9 is typical of that obtained for mixtures when the two components are of similar character (in this case, two hydrocarbons). The highest pressure for mixtures of the two components is much higher than the critical pressure of either one, while the temperatures are generally intermediate. For mixtures of differing substances other shapes have been observed; the experimental material is too limited to permit of generalization.

If a point within the surface be taken—say the point *X*, Fig. 9—there must be two layers for the pressure, temperature and composition corresponding to this point. If from *X* the line of constant pressure and temperature be drawn, it will cut the surface at two points, *Y* and *Z*. These two points give the composition of the two layers, as may be shown from the phase rule or derived directly from thermodynamics. If now a line such as *YZ* be imagined to be moved upward, without change of direction, the points at which it pierces the surface will move closer together; that is, the liquid and vapor layers will differ less and less. Finally, just as the line ceases to pierce the surface the two points will coincide. At this point the liquid and vapor layers will be identical, and this is, therefore, the critical point for the particular composition at which the line just grazes the surface. If, therefore, a line in the direction of constant pressure and temperature be passed along the surface so as just to graze it, the point of contact will trace out the locus of all the critical points for all possible mixtures. It may be seen, therefore, that the critical point may lie on one side or the other of the border curve, depending on the composition of the mixture and the shape of the whole surface.

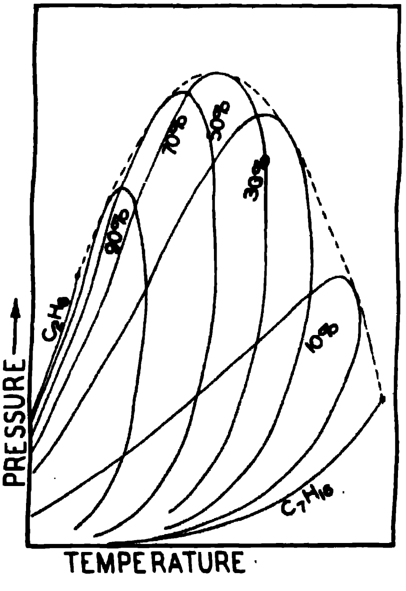

FIG. 10.

The border curves for several mixtures of ethane and *n*-heptane. The dotted curve, or critical envelope curve, is the locus of the critical points of all mixtures of the two substances. This curve usually possesses a maximum-pressure point for hydrocarbon systems.

Another way of considering the aggregate of border curves for all mixtures of two components is to plot all the border curves on one pressure-temperature diagram. Then the envelope of all the curves is the locus of the critical points. Fig. 10 shows certain border curves of the system ethane-heptane plotted in this way

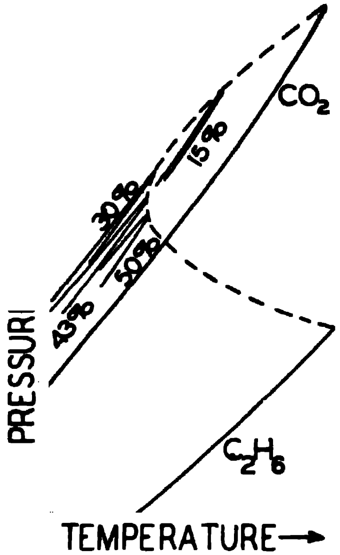

Fig. 11.

Some border curves and the critical envelope curve for the carbon dioxide-ethane system. This is a case where the critical envelope curve has a minimum-temperature point.

Fig. 11 shows a similar plot for the system carbon dioxide-ethane, described by Kuenen. It will be noted that the position of the curves is quite different for this case, but the foregoing statement still holds true.

Density Relationships; the Pseudo-critical Point

While experimental data on the border curves of mixtures are limited, data on the density relationship for mixtures, in the homogeneous region, are almost non-existent. The following statements are based on what data are available, but they cannot be regarded as more than probable.

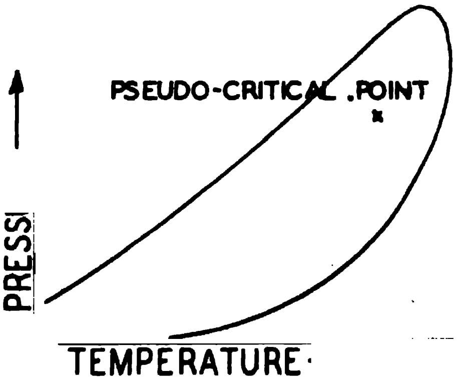

Fig. 12.

The pseudo-critical point is a hypothetical point located somewhere within the border curve of a mixture. It is useful for correlating the pressure, volume and temperature relations of the mixture, outside of the border curve, with those of a pure substance.

Outside the conditions represented by the border curve, the behavior of mixtures (with regard to density as affected by temperature and pressure) does not differ appreciably from that of pure substances. Each mixture behaves as if it were a pure substance with a given critical temperature, pressure and density. When this critical temperature and pressure, obtained by a study of the homogeneous vapor, is plotted on a pressure-temperature diagram, it is found that the point thus determined lies *within* the border curve. An example from the system ethane-heptane is shown in Fig. 12. This point has been called the pseudo-critical point.

Summary of Critical Relations for Mixtures

The critical point of a pure substance possesses four properties, each of which is possessed by a different point in the case of mixtures.

(1) It is the point of highest temperature at which two layers can exist. In a mixture this point is the point of maximum temperature (farthest to the right) on the border curve.

(2) It is the point of highest pressure at which two layers can exist. In a mixture this point is the highest on the border curve.

(3) It is the point at which the density of the liquid and vapor become the same. In a mixture this point is the critical point proper.

(4) It is the point from which the reduced temperature, pressure, and density are computed, for determining the density in the homogeneous region. In a mixture, this point is the pseudo-critical point.

Application of Critical Data

A knowledge of the liquid-vapor relationships is always necessary in the study of distillation, which depends on the difference in composition of liquid and vapor. The pressure and temperature at which distillation can be conducted is limited by the border curves, since it depends on the existence of both liquid and vapor. On the other hand, a surface such as that of Fig. 9 indicates that some separation can be made by distillation at pressures greater than the critical pressure of either component, though pure materials cannot be obtained in this way. Distillation near the critical point is of interest, for example, in the petroleum industry and in the separation of air into its constituents.

It is obvious that in many processes operating under high pressure the design of equipment will be affected by the density of the fluid being handled, since this will determine the size of pipe lines, reactors, and the like. A knowledge on the one hand of the state of the fluid (whether liquid or vapor) and on the other of the density of a homogeneous mixture, can be obtained if the border curve and the pseudo-critical conditions, respectively, are known.

Unfortunately, experimental data in this field are far too limited. There is much need for further work on selected systems, as well as a study of the resulting data to develop means for predicting the behavior of mixtures in the critical region from the behavior of the components, which is relatively well known or easily obtained.

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Measurement of Metal Temperatures of Cracking Still Tubes

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The cracking of oil at temperatures in excess of 900 °F under high pressures has not only called for accurate knowledge of the oil temperatures in a given system, but has also necessitated devising means of procuring the wall or skin temperatures of the tubes in which the conversion is taking place.

Cracking still tubes used today vary in diameter, length, wall thickness, and composition of metal. Diameters are fairly well determined to accommodate velocities or heat absorption rates in any portion of the heater. Upon type of material selected depends the ultimate strength of the tube as well as its resistance to wear and corrosion. In many processes tubes between four and five inches O. D. with three-eighths to one-half inch walls are used, so we shall confine our discussion to these sizes. Materials used, on the other hand, range all the way from ordinary carbon steels through the low chromes and on to KA2S. In many instances low percentages of molybdenum or tungsten are incorporated in these alloys to serve as stabilizers, definitely adding to the strength of the finished tube. Silicon in small proportions presents a claim for resistance to both oxidation and corrosion.

Our particular problem was confined to devising a system of attaching temperature-measuring elements to the fire side of five-inch by four-inch alloy tubes, 45 feet in length, and arranged in two concentric rows in a 30-foot diameter vertical heater. Each heater or furnace contains about 150 of these tubes, and is fired from the top through one circular-shaped, multi-port burner. In furnaces of this type, heat is supplied to the oil substantially by radiation.

The inner row of tubes (nearer the fire) is placed about thirteen feet from the vertical axis of the heater, with the second or outer row ten inches nearer the furnace wall. Under normal conditions no flames impinge on or approach the tube surface, and because of the high heat transmission rate through the tube walls into the oil, the furnace atmosphere in the vicinity of the tubes is cooled to a temperature of between 1300 and 1400 °F, as measured by furnace pyrometers arranged at 90° intervals around the heater.

Pressure in the tubes varies from 1000 psi at the inlet to 400 psi at the outlet. Pressure taps placed at intermediate points serve to define fairly well the pressure at any tube in the system. Then from a combined knowledge of pressure, I. D. or wall thickness, and allowable creep stress of the tube material at various temperatures, we can plot corresponding values and from the curve quickly determine optimum safe working conditions.

It will be noticed that the lines do not extend above the 1200 °F ordinate. This is because allowable stresses above this point are too low for practical use in this particular field. Furthermore, once metal temperatures approach 1200 °F, it is probably because a heavy coke deposit has accumulated on the inside of the tubes, thus making continued operation impractical.

In certain types of heater it is possible for the operator to determine the presence of overheated tubes by visual inspection through peep-holes in the furnace walls. Clean tubes naturally allow the heat to be transferred to the oil on the inside, with the result that temperature differential between outside wall and oil is kept at a minimum. Tube walls appear black or "dead" wherever temperature does not exceed 1000-1050 °F, while above that range they begin to show a glaze or color. Where blackbody conditions exist, it is conceivable that tube temperatures can be closely gaged by simply noting tube color, but in radiant-heat furnaces there is no opportunity to make this correlation. There does exist, however, a perceptible difference between "cold" and hot tubes, but the degree of hotness is not discernible to the naked eye.

As previously stated, our particular problem was to find an accurate and suitable method of attaching temperature-sensitive elements to four-inch and five-inch O. D. tubes, arranged vertically in a radiant-heat furnace. The steps taken and progress achieved was probably not unlike that of others in the oil industry whose problem differed only because of variation in furnace design and method of firing.

After the first radiant heaters were built, it took but a short time for all concerned to agree that visual inspection for over-heated tubes was of no value. Available at that time was a Perfection pyrometer, supposedly capable of measuring the temperature of any object upon which it was properly focused. This instrument was limited as to range, especially when the sighted object was but four inches across and 18 to 30 inches away. Furthermore, it was possible to sight only on the back or cooler side of the tube, which was not subjected to direct radiant heat. The principle upon which this instrument operates is identical with that of the burning glass, whereby the light and heat rays are focused from a steel reflector onto tiny thermocouples arranged in series, and the resulting emf deflects a galvanometer. Recent developments tending toward increasing the focal powers of the sighting tube and overall sensitivity and accuracy have made this pyrometer useful in many fields.

The possibility of utilizing a small thermocouple pressed against the surface of the tube was also tried. Insulated iron and constantan wires were encased in half-inch pipe and terminated at the fire-end as a ribbon pulled taut over a lava block, shaped to fit the curvature of the tube. The emf developed was indicated on a millivoltmeter. This instrument, like its predecessor, indicated only the temperature of the cooler side of the tubes, and at best the readings were only relative. Even though the operators were inclined to doubt its accuracy, the readings as taken did serve as a means of warning to them.

About this time cracking still technic had become developed to the point where runs of 100 days' duration were quite common. To secure maximum output and efficiency from a given unit required that firing rates be stepped up, with the consequent danger of overheating the tube walls. Relative or inaccurate tube wall temperature could no longer be countenanced. The only suitable method appeared to be that of attaching or peening couples on the fire side of those tubes subjected to the most severe conditions, and then providing suitable protection for the wires against high temperatures and corrosive action. Because of the oxidizing atmosphere, iron could not be used as one of the wires. Attaching a complete couple by peening two wires into the tube presented the problem of properly insulating in the vicinity of the junctions against heat conduction along the wires to the couple. However, two-wire systems of KA2S and Chromel are in use today; any error due to heat conduction mentioned above is accepted as a safety factor.

The application consists of drilling two one-eighth-inch holes one-eighth inch deep into the face of the tube. After the porcelain bead or other type insulators have been threaded on the wires, and the wires (No. 8 B. & S. gage) bent to fit the circumference of the tube, the peening or fastening into the drilled holes is done. The two No. 8 wires are extended through the furnace wall and terminate in a thermocouple head. From this point to the indicator or recorder No. 14 gage wires are used.

The method of attaching and protecting the wires described above is but one of the many in use today. A few of the companies persisted in the use of complete two-wire systems, adding improvements as they went along, until today they have adopted it as their standard and consider the results accurate and the cost of upkeep within reason.

The use of a single wire peened into a tube with the second wire junction remaining in a cold space seemed to us, at least, to offer the best possibilities. Starting with No. 8 constantan as the hot wire, the most difficult problem was to find an adequate system of protection for that wire against high temperature and oxidation. It was equally essential that the protector serve as one of the wires for the couple inside the furnace wall. Properly coated steel tubing was selected as the logical substance to use, since it could easily be welded to the alloy tubes and permit the use of available iron-constantan-calibrated potentiometers.

To begin with, the constantan wire is wrapped with two layers of three-ply one-sixteenth-inch diameter asbestos string, and coated with high-temperature shellac. It is then placed inside a protection tube made by Calorizing specially prepared (pickled) half-inch seamless steel tubing, which had previously been bent in the form of a shepherd's crook. The end of the curved portion is belled to fit the curvature of the tube to allow welding area and to give good electrical contact.

The application of the wire and protector to the tube consists of inserting the squared end of the wire into the one-eighth-inch-deep hole in the tube and peening by the use of a specially shaped tool adapted for use with a pocket-size air hammer. Much depends on a perfect peening job, since a loose connection at this junction will greatly shorten the true-reading life of the couple. The next operation consists of applying additional asbestos wrapping to the wire immediately adjacent to the heater tube. This is applied in a cone shape to match the spread produced by belling the end of the protector. Such additional asbestos serves a dual purpose: it insures against electrical short circuiting as well as insulates against heat conduction to the peened joint. The belled end of the protector is then pressed tight against the heater tube and welded. This junction is later tested for pressure-tightness to make certain that corrosive flue gases do not come into contact with the peened junction.

Outside the furnace wall a short piece of No. 12 or No. 14 iron wire is peened into the end of the Calorized tube. This wire, together with the No. 8 constantan, terminates in a standard thermocouple head, from which No. 14 wires of the proper material extend to the switch panel.

To allow for the downward movement of the tubes due to expansion by heating, the hole in the heater casing through which the protection well extends is slotted for a distance of three inches. This allows the protector to move freely without binding, its only support being the weld at the crooked end.

The number of heater tubes to which skin-temperature thermowells must be attached naturally depends a great deal on the design of the furnace and arrangement of tubes therein. In some instances every tenth or twelfth tube has a couple attached, so for large cracking units as many as sixty couples are required and are read from a common switch panel. Our practice has been to use a special switch arrangement whereby several of the highest readings, taken periodically by the operator, can be thrown onto potentiometer recorders in the main control room.

The foregoing method of applying tube-wall thermocouples in radiant-heat cracking and topping furnaces has proved satisfactory over an extended period of time. The Calorized tubing resists both the heat and corrosive action of the furnace gases, and, with a good bond at the peened joint, the readings as taken are considered reasonably accurate for a period of a year or more.

A Theoretical Study of the Design of Thermocouples for Experimental Cracking Units

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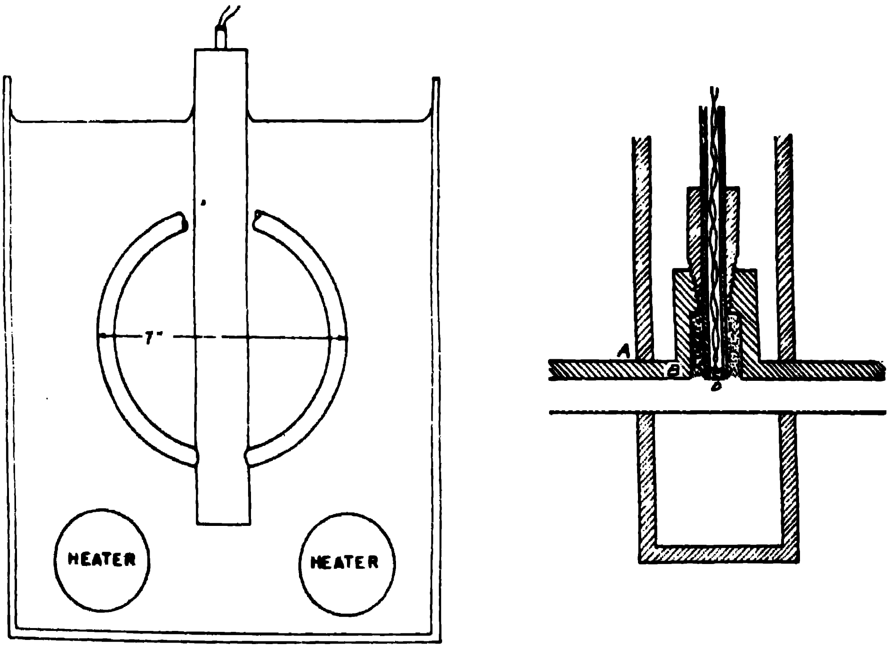
Experimental cracking units whose heating element consists of a lead bath containing a spiral steel tube are widely used. They are convenient to operate because of the ease with which the cracking coils may be changed, and also because the temperature control of the lead bath is simple and definite. In most cases the final temperature of the oil will be substantially that of the lead bath, but there will, of course be a difference between lead and oil temperature in the first part of the tube where the oil is heating. The present paper is concerned with thermocouples used to determine this temperature difference.



End view of pencil-type thermocouple assembly in lead bath.

Cross-section through thermocouple.

FIG. 1. Pencil-type thermocouple used to indicate oil temperature in coils immersed in lead baths.

The assembly first used to measure the oil temperature is shown in Fig. 1. A pipe coupling was welded into the tube at the bottom of one of the turns. Into the coupling was screwed a pencil type thermocouple which extended down to the edge of the oil stream, it being important not to have the thermocouple project into the stream because of the possibility of eddy currents favoring coke deposition which might eventually cause a stoppage of the oil flow. A 1½-inch vertical jacket welded about the assembly kept the lead from getting into the pipe threads.

After this couple had been in use for a while, the question was raised as to whether it did actually show the differential in lead-oil temperature, or whether conduction in from the lead caused it to read closer to lead temperature than to the oil temperature. Calculations of the extent to which the thermocouple is in error must necessarily be only approximate; nevertheless they should aid in evaluating its reliability. Estimates of the thermal resistances from various points of the assembly to other points were made and are given in Table 1. The thermal conductivities given there are taken from Perry's "Chemical Engineers' Handbook," first edition, pages 826 and 828. The film coefficient is calculated from the chart given in Walker, Lewis, McAdams and Gilliland's "Principles of Chem-

Table 1. Estimates of Thermal Resistances between Points Shown in Fig. 1.

Basis of Calculations

Dimensions:

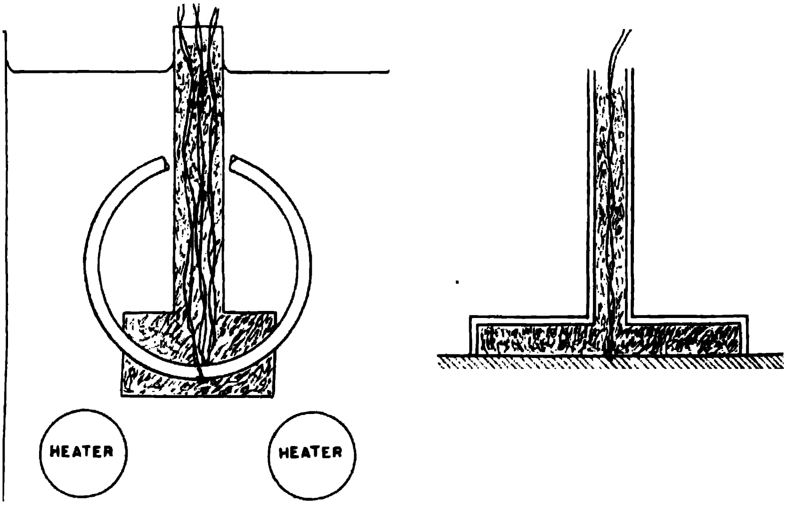
Cracking Coil	3/16" I.D. × 9/16" O.D.
Coupling	1/2" I.D. × 7/8" O.D.
Thermocouple Pencil	3/16" I.D. × 5/16" O.D.
Jacket	1.610" I.D. × 1.900" O.D.

Thermal Coefficients (at 1000 °F):

Conductivity of iron	22 Btu/ft^2 × hr × (°F/ft)
Conductivity of coke	2.9 Btu/ft^2 × hr × (°F/ft)
Film Coefficient	103 Btu/ft^2 × hr × °F.

Thermal Resistances

From	to	
A	B	.553 °F/(Btu/hr)
B	C	.985
A	C	1.54
C	D	18.2
A	D	19.7



End view of coil with thermocouple jacket in lead bath.

Cross-section of thermocouple jacket.

FIG. 2. Thermocouple assembly proposed for measuring oil temperatures in coils immersed in lead baths.

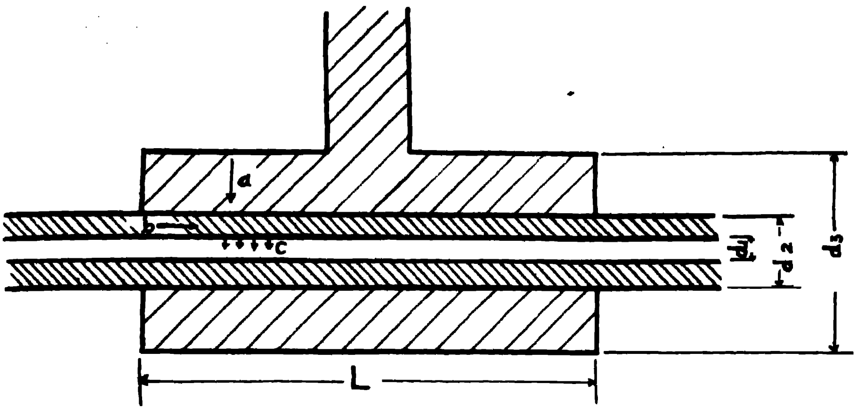


FIG. 3. Calculation of correction factor for proposed thermocouple assembly.

a = thermal conductivity through insulation

$$= \frac{2\pi k_i}{2.3 \log d_3/d_2}$$

b = thermal conductivity along tube

$$= \frac{\pi}{4}(d_2^2 - d_1^2)\, k_{Fe}$$

c = thermal conductivity to oil

$$= \pi\, h\, d_1$$

f = correction factor = ratio of the actual to the observed difference in lead to oil temperature

L = length of lagged section

To get f for a given couple

$$P = L\sqrt{\frac{a+c}{b}}$$

Find corresponding value of Q from Fig. 4

$$f = \frac{a+c}{c} \times \frac{1}{Q}$$

k_i = thermal conductivity of insulation

k_{Fe} = thermal conductivity of tube metal

h = thermal film coefficient of oil

To get L required for given f

$$Q = \frac{a+c}{c} \times \frac{1}{f}$$

Find corresponding value of P from Fig. 4

$$L = P\sqrt{\frac{b}{a+c}}$$

ical Engineering," page 112 (flow was 2650 cc/hr, viscosity 0.07 centipoise at 1000 °F). The thermal resistance across the coke bridge was calculated by dividing it into a number of horizontal sections, determining the resistance through each including the metal path leading to and from it, and adding all these resistances in parallel.

Considering the various thermal resistances given in Table 1, it is immediately apparent that the annular space which was intended to protect the couple from heat flow in from the lead is ineffectual. We may take as the correction factor the ratio of the true difference between lead and oil temperature to that indicated by the thermocouple assembly. This ratio may also be expressed as a function of the resistances:

$$\text{Correction factor} = f = \frac{\text{resistance from } A \text{ to } D}{\text{resistance from } A \text{ to } C}$$

$$\text{which in this case} = \frac{19.7}{1.54} = 13.$$

Thus for this assembly the observed temperature difference should be multiplied by 13 in order to get the actual difference between lead and oil temperature. However, the foregoing calculations were made on the assumption that the annular space was completely coked up. If this is not the case, the resistance through the annular space will be greater, and that from the couple to the oil will be lower. Taking as an extreme case a situation where 60 per cent of the annular space is coked up and the other 40 per cent contains oil having the same temperature and thermal film coefficient as the main body of the oil, the calculation shows that the coke bridge still has less resistance than other parts of the thermal circuit, the correction factor being about 2.5.

Since the coke bridge has a low resistance and the oil film at the end of the couple a high one because of its small area, it appeared that a thermocouple peened to the outside of the tube and protected from the lead by a short section of lagging might give better results. Fig. 2 shows this type of assembly. The lagging and thermocouples, one active and two spares, are protected from the lead by a welded steel box. This assembly has the advantage of having a large area of metal near the couple exposed to the oil. The correction factor for this assembly is related to length of the insulated region by the equation:

$$L = 4.6 \frac{}{a + c} \log \frac{f \cdot \quad a + c}{f - \sqrt{f^2 - \left(f - \frac{a + c}{c}\right)^2}}$$

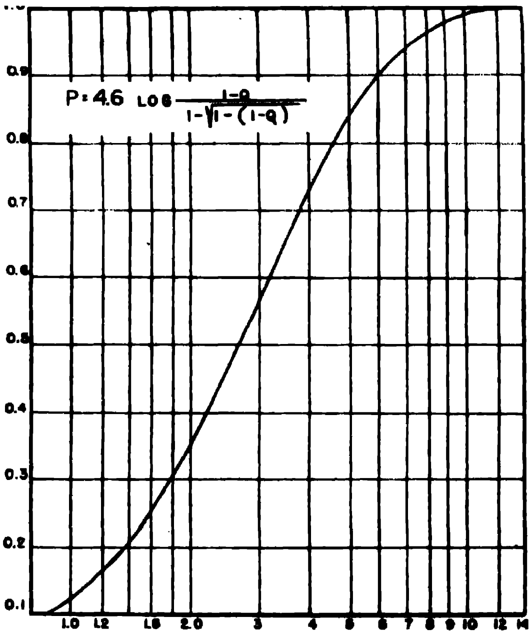


FIG. 4. Curve for determining P or Q, one in terms of the other, for use in Fig. 3.

(The definitions of the terms involved are given in Fig. 3.) This equation may be simplified by defining two dimensionless factors, P and Q:

$$P = L\sqrt{\frac{a + c}{c}}$$

$$Q = a + c\ 1$$

Then

$$P = 4.6 \log \frac{1 - Q}{1 - \sqrt{1 - (1 - Q)^2}}$$

This equation holds for all assemblies of this type, and is plotted in Fig. 4 to permit ready evaluation of either when the other is known. The method of determining f for a given assembly, or the length, L, required to give a certain value of f for an assembly, is outlined in Fig. 3.

As an illustration, consider a cracking coil of the same dimensions and under the same conditions that were used as a basis in Table 1.

$d_1 = 0.0156$ ft
$d_2 = 0.0468$ ft
$d_3 = 0.130$ ft
$L = 0.500$ ft

$K_{Fe} = 22$ Btu/ft^2 × hr × (°F/ft)
$K_i = 0.1$ Btu/ft^2 × hr × (°F/ft)
$h = 103$ Btu/ft^2 × hr × °F

Then from Fig. 3

$$\frac{2\pi \times 0.1}{2.3 \log \dfrac{0.130}{0.0468}} = 0.617$$

$$b = \frac{\pi}{4}[(0.0468)^2 - (0.0156)^2] \times 22 = 0.034$$

$$c = \pi \times 103 \times 0.0156 = 5.05$$

$$P = 500\sqrt{\frac{5.05 + 0.617}{0.034}} = 6.44$$

From Fig. 4, for $P = 6.44$, $Q = 0.923$

$$f = \frac{5.05 + 0.617}{5.05} \times \frac{1}{\text{[illegible]}} = 1.22$$

Table 2. Effect of Design Variables and Thermal Coefficients upon the Correction Factor of the Proposed Thermocouple Assembly.

Variable	Tubing		Insulation		Thermal Coefficients			f
	I.D. (In)	O.D. (In)	Thickness (In)	Length (In)	K_i Btu hr×ft^2×(°F/ft)	K_{Fe} Btu hr×ft^2×(°F/ft)	h Btu hr×ft^2×°F	
h	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	50	1.55
h	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
h	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	200	1.09
h	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	500	1.03
d_1 and d_2	$\frac{1}{16}$	$\frac{3}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
d_1 and d_2	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
d_1 and d_2	$\frac{1}{4}$" X.H. Pipe about $\frac{6}{16}$" × $\frac{10}{16}$"		$\frac{1}{2}$	6	0.1	22	100	1.10
L	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	3	0.1	22	100	1.86
L	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
L	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	12	0.1	22	100	1.13
d_3	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
d_3	$\frac{3}{16}$	$\frac{9}{16}$	2	6	0.1	22	100	1.16
K_i	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.2	22	100	1.35
K_i	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.1	22	100	1.22
K_i	$\frac{3}{16}$	$\frac{9}{16}$	$\frac{1}{2}$	6	0.02	22	100	1.13

Thus an assembly lagged with six inches of half-inch diatomaceous earth gives a correction factor of about 1.2 as compared to a factor of anywhere from 2.5 to 13 for the pencil couple assembly described above. A further advantage of the present couple is that a small layer of coke inside the tube will have very little effect upon the correction factor, because although the thermal resistance of the wall is increased, this effect is offset when one is using small tubes, since the higher velocities resulting from a decrease in diameter improve the film coefficient.

The change in correction factor which corresponds to various changes in design or in thermal coefficients is shown in Table 2. For most cracking work, where h has a value of 100 Btu/hr $\times$ ft^2 $\times$ °F or above, a jacket with six inches of diatomaceous earth one-half inch thick should suffice. Assemblies of this type have been in use in the research laboratories of The Atlantic Refining Company for some time, and are very satisfactory from an operating viewpoint.

Temperature Control Reduces Oil Storage Losses

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Twenty years ago the world was faced with a petroleum shortage. During the war and shortly thereafter, the consumption of refined products exceeded the production of crude oil. This situation stimulated exploration to such an extent that proved reserves have mounted steadily ever since. At the start of 1939, the estimated reserves for the entire world amounted to 34 billion barrels. Half of this amount, 17 billion barrels, lies within the United States.

Although the United States is no longer in any danger from an immediate shortage, the conservation of our oil resources is a matter of vital concern. Petroleum derivatives now play an essential part in almost every phase of man's activity. In a broad sense, conservation involves exploration for new fields, protection of known reserves, improvements in transportation and storage, increased efficiency in refining processes and mechanical perfection of devices utilizing petroleum products. This paper deals with conservation only in its relation to storage problems.

The continuous flow of fuels and lubricants required by modern factories and motor vehicles can be maintained only by providing adequate storage facilities at key points in the producing, refining and distributing branches of the oil industry. The universally accepted unit for the retention of volatile liquids is the steel storage tank. Such tanks are expensive, both in first cost and in the cost of operation.

The tendency of any petroleum product to vaporize is directly proportional to its vapor pressure. The vapor pressure depends upon the physical characteristics of the liquid and its temperature. During the day, rising temperatures cause the surface liquid in the storage tank to vaporize, expand and seek relief through the roof vent. In this way, daily temperature variations reap a tremendous toll from the oil industry in the form of evaporation losses. These losses constitute the greatest single item of expense in the cost of operating a storage tank.

Petroleum is a complex mixture of hydrocarbons. When it is heated, these hydrocarbons are distilled off one at a time in the order of their respective boiling points. When vaporization occurs in a storage tank, the lighter fractions tend to evaporate first just as they would in the distillation process. Some of the hydrocarbons found in crude oil have a much greater value than others. In general, those utilized in the manufacture of motor fuels are worth the most. In the older refining methods, gasoline was derived from crude oil by straight distillation and the lighter fractions, such as butane and propane, formed no part of the finished product. Consequently, no one was much concerned over the loss of these constituents by evaporation from crude oil in storage.

Today, the situation has changed. Encouraged by the growing demand for 100-octane aviation gasoline and other premium fuels, petroleum chemists and engineers have recently developed unit processes capable of turning these products out on a commercial scale.

Significant facts relating to these processes are outlined in Table 1. Oddly enough, the essential raw materials for several of them are the light fractions

Table 1. Operating Features of Some of the Important Processes in the Petroleum Industry*

	Cracking		Polymerization		Hydrogenation	Dehydrogenation	Alkylation	Isomerization
	Thermal	Catalytic	Thermal	Catalytic	Catalytic	Catalytic	Catalytic	Catalytic
Process (all in commercial operation)	*Liquid phase* Dubbs Cross deFlorez Holmes-Manley Tube & Tank Combination Uni-Coil *Vapor phase* True Vapor Phase Alco and Gyro	Houdry U.O.P. Catalytic Ref. Group (S.O. of N.J., S.O. of Ind., German I.G. & M.W. Kellogg).	Alco-Pure Oil Unitary (Polyco) Multiple Coil	U.O.P. Selective U.O.P. Non-selective Houdry Polyco Shell Iso-octane	S.O. of N.J. U.O.P. Shell	U.O.P. Shell	S.O. of N.J. Shell The Texas Co. A.I.O.C. Humble S.O. of Ind. U.O.P.	U.O.P. Shell
Catalysts	....	activated clays (natural and synthetic)	....	phosphoric acid hot sulfuric acid cold sulfuric acid	activated nickel metal oxides	aluminum and chromic oxides	sulfuric acid aluminum chloride boron fluoride	aluminum chloride
Reaction temp. (°F)	850-1,100	800-1,000	1,000	175-400	500-1,000 400	1,050	35-100	200
Reaction press. (lb/sq in)	50-1,500	atm-200	600-2,500	150-1,500	1,500-4,500 60-100	atm	about atm	200

Chemical and Metallurgical Engineering, August, 1939

Raw materials	high-boiling petroleum fractions	gas oil reduced crude	propane propene buanes butenes	propene butenes	unsat. hydrocarbons	butanes propane	iso-butane plus butane	*n*-butane *n*-pentane
Products	gases: C_1, C_2, C_3, C_4, sat. and unsat. gasolines fuel oil	gases gasoline gas oil fuel oil	high-octane gasolines (many olefines)	high-octane gasolines	saturated hydrocarbons	butenes propene	iso-octane	iso-butane iso-pentane
Capacities (bbl. per day throughput)	500-35,000	3,000-18,000	1,000-10,000	50-5,000	1,000-10,000	450-1,000	1,000-2,500 product	?
Yields (per cent)	Depends on charging stock, conditions and catalyst.		45-55	Almost theoretical on isobutene. Others depend on product.	95 on hydrogen	90	100	70-80
Octane number obtainable	67-80	78-82	75-80	80-85	90-100 depending on charging stock	....	90-100	Process used to prepare charge for alkylation

which were formerly allowed to go to waste. Companies operating modern refining units can no longer afford to tolerate the loss of these now valuable light ends. Neither can they afford to store valuable finished products in containers which permit excessive evaporation loss and the attendant decrease in vapor pressure and loss of octane rating.

Evaporation losses can be held to a minimum by a well-balanced line of storage equipment consisting of crude oil tanks capable of preserving the light ends in the oil in liquid form, pressure vessels for storing these constituents after their separation from the crude oil, and finished-product tanks designed to store premium fuels for indefinite periods of time without loss in vapor pressure or octane rating. Before discussing the design of special storage tanks, let us consider the phenomena responsible for losses from a conventional type of storage tank, that is, a cylindrical tank having a fixed roof equipped with relief valves designed to vent inwardly or outwardly at a partial vacuum or pressure not exceeding a value of about 1 oz per sq in. The stored product is any volatile liquid whose vapor pressure is not high enough to cause boiling at normal storage temperatures.

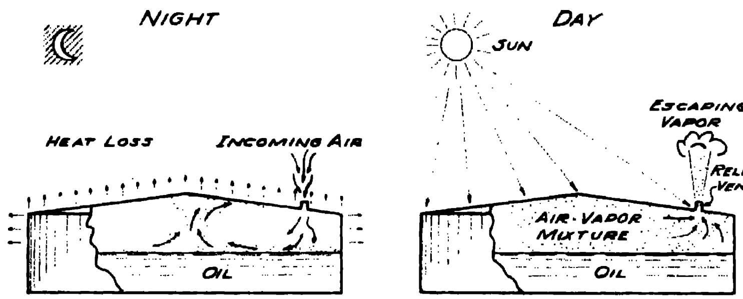

FIG. 1. Daily tank breathing cycle.

The normal daily breathing cycle for such a tank is illustrated in Fig. 1. When atmospheric temperature falls during the night, the tank vapors cool and contract, which causes air to be drawn in through the roof vent. As heat is lost from the tank through the roof and shell, convection currents are set up in the vapor space. These currents whip up the vapors at the liquid surface, thereby mixing them with the incoming air. On the following day the tank absorbs solar heat through the roof. This increases the rate of vaporization at the liquid surface and causes the air-vapor mixture to expand and seek relief through the roof vent. Vapor losses of this sort caused by the daily temperature cycle are called breathing losses.

Typical curves illustrating the daily temperature variations at different points in an 80,000-bbl storage tank containing stabilized casinghead gasoline are shown in Fig. 2. An idea of the economic significance of the losses resulting from these temperature changes may be obtained from the following example: An 80,000-bbl motor gasoline tank equipped with the usual conservation vents will suffer an average yearly breathing loss of approximately 100,000 gallons. This volume of motor fuel, if saved, would be sufficient to propel an automobile about 1,500,000 miles or 60 times around the earth. Losses of this magnitude merit serious consideration.

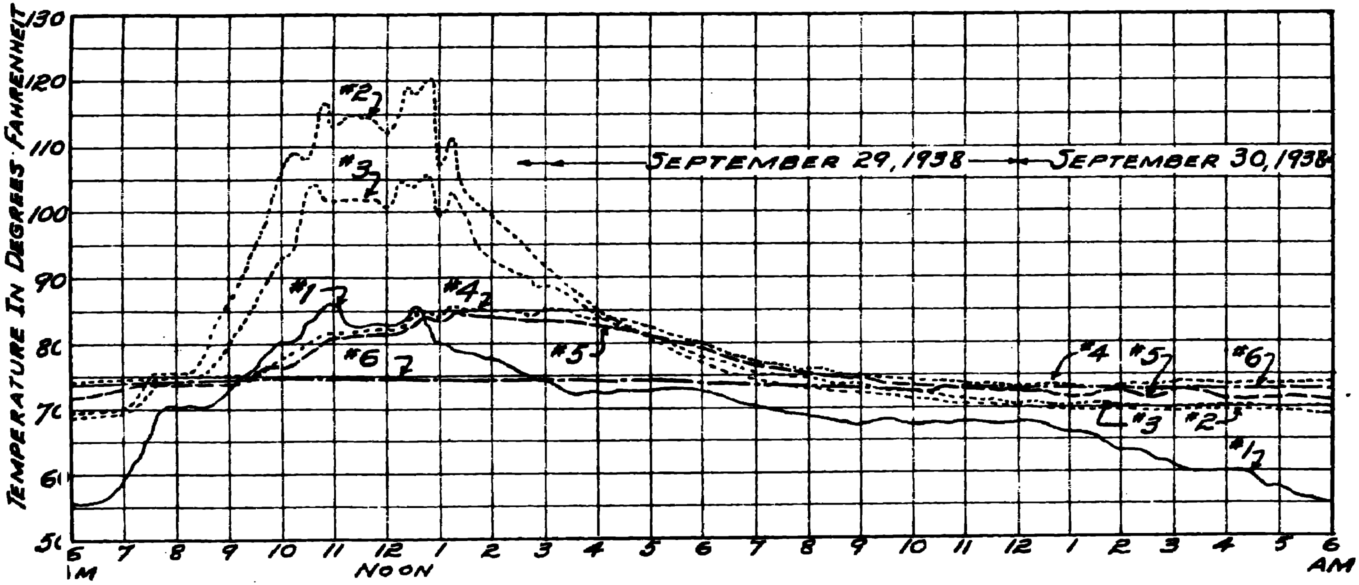

FIG d ca: ga:

Cu: 1, Atmosphe
Cu: 2, Top of vapor space
Cu 3, Middle of vapor spa

Curve 4, Vapor space, -- ' above 'ace of
Curve 5, Oil, $\frac{3}{16}$" below surface
Curve 6, Oil, 5' 9½" below surfac

The methods which may be utilized in reducing breathing losses are as follows:

(1) reduction of temperature variations within the tank;
(2) complete elimination of the vapor space;
(3) use of a variable vapor space;
(4) pressure storage.

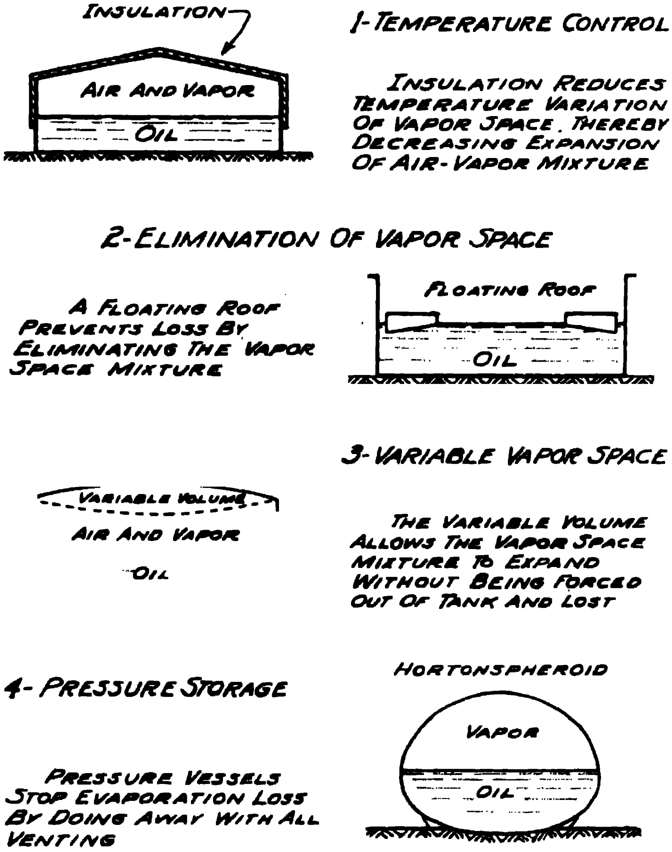
Insulation
1-Temperature Control
Air And Vapor
Oil
Insulation Reduces Temperature Variation Of Vapor Space. Thereby Decreasing Expansion Of Air-Vapor Mixture
2-Elimination Of Vapor Space
A Floating Roof Prevents Loss By Eliminating The Vapor Space Mixture
Floating Roof
Oil
3-Variable Vapor Space
Variable Volume
Air And Vapor
Oil
The Variable Volume Allows The Vapor Space Mixture To Expand Without Being Forced Out Of Tank And Lost
4-Pressure Storage
Hortonspheroid
Vapor
Oil
Pressure Vessels Stop Evaporation Loss By Doing Away With All Venting

FIG. 3. Methods for reducing breathing losses.

The more common types of storage containers used in the application of these methods are illustrated in Fig. 3, and the practicability of each is discussed in the following paragraphs.

Direct Temperature Control

Breathing losses, being the direct result of temperature changes, can obviously be reduced to a certain extent by providing an insulating medium which will decrease the magnitude of the vapor space temperature variations. Most of the earlier attempts to minimize vapor losses followed this line of reasoning, and some of the schemes that were put into practice are shown in Fig. 4. One method of insulating consisted of carrying several inches of water on a flat vapor-tight steel roof. This did cool the contents of the tank but it also caused the roof plates to rust out rapidly. The water-spray system provided a second and more efficient means of cooling, but such systems were rather expensive to operate and the water tended to cause deterioration of the roof and shell plates.

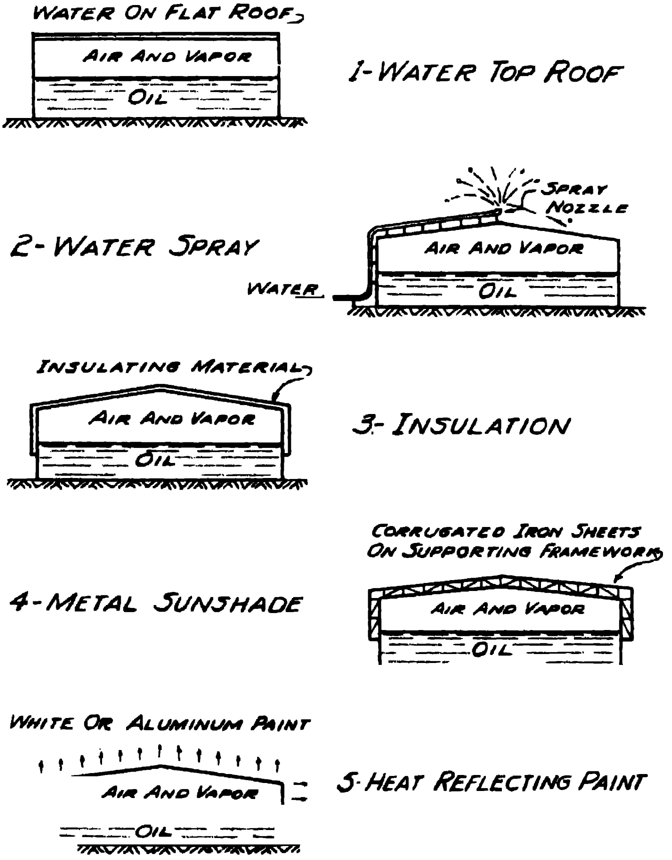

FIG. 4. Various schemes for reducing vapor-space temperature variations.

A third method consisted of covering the roof and most of the shell with a layer of insulating material. This was more satisfactory from the operating standpoint, but the reduction in breathing loss which it effected was not sufficiently great to justify the initial expenditure for insulation. A fourth method involved the construction of a metal hood or sunshade over the tank. An installation of this type is usually too expensive to be justified by the results achieved.

The fifth scheme for reducing temperature changes within the tank consists of the application of a light-colored heat-resisting paint to the exterior surface of the roof and shell. This method has found almost universal application because tanks must be painted anyhow to protect the steel. It is common practice to use an aluminum paint or a free-chalking white paint, either of which will effect a noticeable reduction in the maximum vapor space temperatures. Light paints are most effective when used in conjunction with other methods of evaporation loss prevention. At best the reduction of temperature changes in an ordinary cylindrical tank will eliminate only a fraction of the breathing loss. For this reason, none of the schemes shown in Fig. 4 can be regarded as a satisfactory solution to the problem. Since direct temperature control will not produce the desired results, it has been necessary to resort to methods of evaporation loss reduction which counteract the effects of temperature changes rather than prevent the changes themselves.

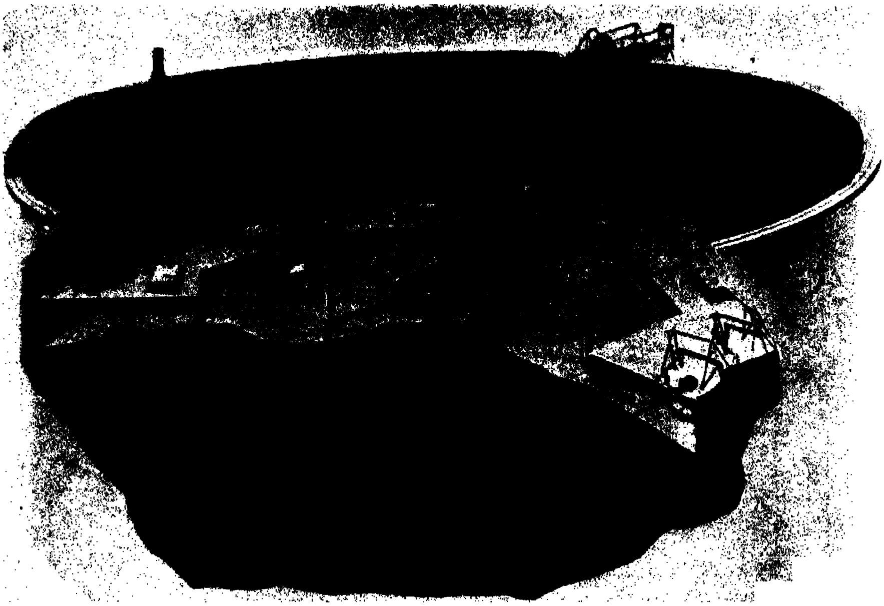

FIG. 5. Pontoon-type floating roof.

Elimination of the Vapor Space

Temperature changes cannot cause vapor losses if the space occupied by the vapor is eliminated. Consequently, breathing losses can be prevented by constructing a storage tank in such a way that no vapor space exists under any condition of operation. This may be accomplished by equipping the tank with a roof which floats on the oil and rides up or down as the tank is filled or emptied. A roof of this type known as the Wiggins pontoon roof is illustrated by the cutaway drawing in Fig. 5. It is made up of a rigid annular pontoon to which is attached a flexible center deck plate. The space between the edge of the roof and the tank shell is sealed by a series of steel shoes connected to the roof by a continuous strip of gas-tight fabric. The shoes are supported and held against the tank shell by hangers attached to the deck of the roof. A special rolling ladder provides access to the roof from the top of the tank shell and a drainage system facilitates the removal of rain-water from the center deck.

During extremely hot weather, the steel plates forming the center deck may become hot enough to cause the liquid in contact with them to boil. Since the bottom of the annular pontoon slopes upward toward the center, the vapor thus formed is trapped and retained under the center deck until nightfall when cooler temperatures cause it to recondense. This feature enables the pontoon roof to operate efficiently under the most severe climatic conditions. By eliminating the vapor space during all stages of filling, the floating roof also eliminates all filling loss, that is, the loss that occurs when vapor is forced out of a fixed roof tank by the incoming liquid during filling. For this reason, the floating roof is especially well adapted to working tanks which are filled and emptied at frequent intervals.

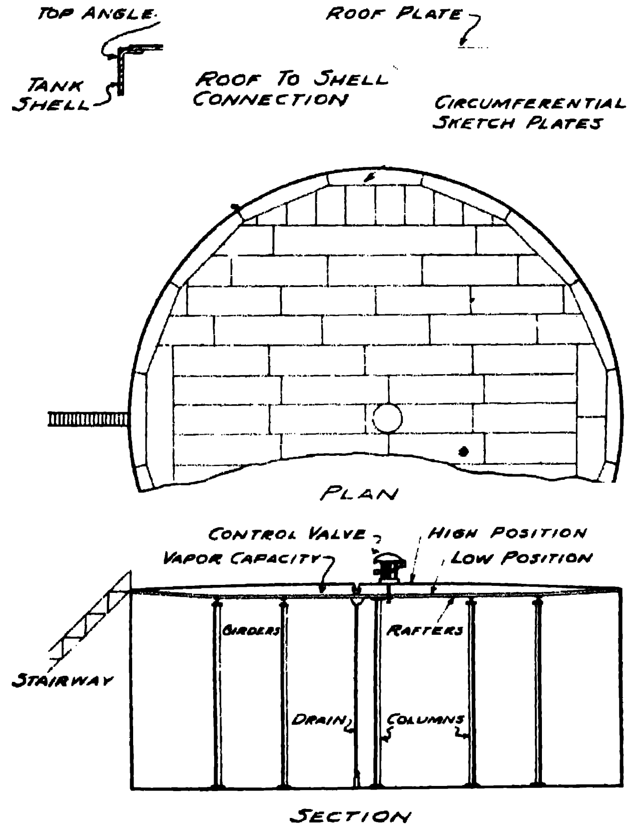

FIG. 6. General plan of Wiggins Breather Roof.

Variable Vapor Space

Breathing losses due to atmospheric temperature change can be prevented by equipping the storage tank with a vapor space whose volume can vary to accommodate changes in the volume of the air-vapor mixture. This allows the vapors to expand without being forced out of the tank and lost. The variable vapor space can be secured by the use of a flexible deck called a breather roof. General details of the Wiggins breather roof are given in Fig. 6. The roof proper is a diaphragm made up of $\frac{3}{16}$-in steel plates welded together. It is attached at its periphery to the top of the tank shell. In its down position, the diaphragm rests on a supporting framing of rafters, girders, and columns. It is not attached to this framing, however, and is thus free to flex upward as the air-vapor mixture in the tank expands.

There is nothing complicated about the operation of a breather roof. As rising temperature causes the tank vapors to expand, the deck plates balloon upward. This increases the vapor space volume and prevents the vapors from being forced out into the atmosphere and lost. At night, when the vapors contract as a result of falling temperature, the roof flexes downward, thereby decreasing the volume of the vapor space and preventing air from being drawn into the tank. The breather roof was developed primarily for use on tanks in standing storage service. Most crude oils and motor gasolines can be stored indefinitely in tanks equiped with breather roofs without volumetric loss by evaporation or deterioration in quality.

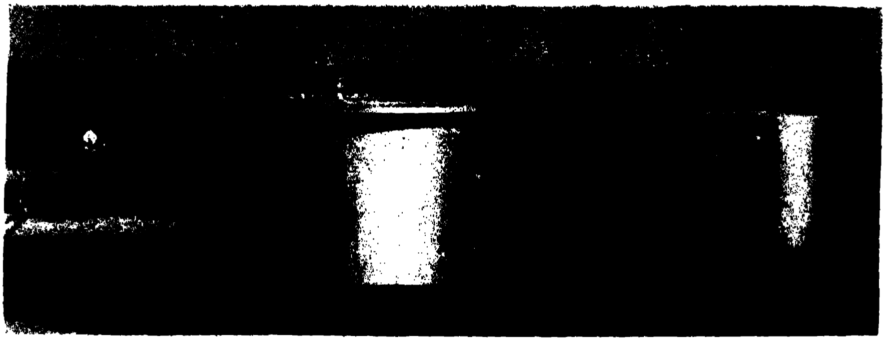

Fig. 7. Balloon roof tank connected to tank with fixed roof.

A similar roof, which operates on the same principle but provides for a much greater variation in vapor space volume, is the Wiggins balloon roof shown in Fig. 7. It is made up of an upper diaphragm extending beyond the tank shell, a shallow vertical rim and a lower extension plate which connects the bottom of the rim with the top of the tank shell. When expansion occurs, this lower plate flexes upward at the outer edge, thus allowing the entire roof to rise. Inasmuch as the balloon roof has a much greater capacity than the breather roof, it is capable of preventing breathing losses from partially filled tanks as well as from those which are filled almost to the top. It is used extensively on tanks at marketing stations and marine terminals which are filled and emptied only a few times per year.

The large vapor capacity provided by a balloon roof also enables it to be used as a gasholder in preventing breathing losses from adjacent tanks with gas-tight fixed roofs. The balloon roof in Fig. 7 is connected by a vapor line to the small tank at the right. Vapors forced out of this tank by temperature variations pass through this line to the balloon roof where they are retained temporarily until changing atmospheric conditions cause their return. This idea can be extended still further by constructing an independent steel balloon on the ground and extending vapor lines from it to a number of tanks with fixed roofs. A system of this kind is illustrated in Fig. 8. Balloon systems are usually installed for the purpose of reducing evaporation losses from groups of existing tanks. Steel balloons have been built in capacities up to 350,000 cu ft, and much larger sizes are practical.

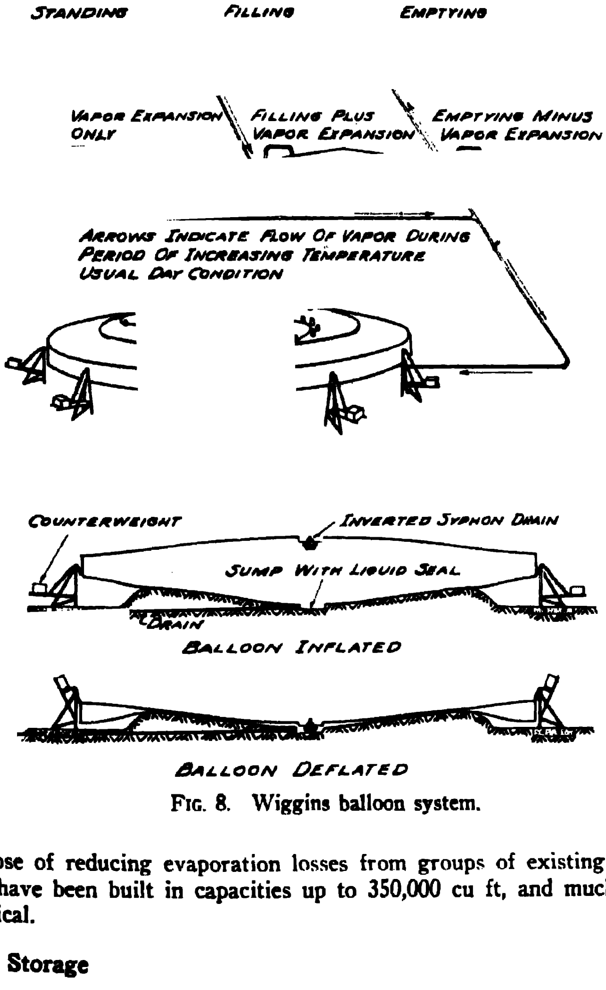
Standing
Filling
Emptying
Vapor Expansion Only
Filling Plus Vapor Expansion
Emptying Minus Vapor Expansion
Arrows Indicate Flow Of Vapor During Period Of Increasing Temperature Usual Day Condition
Counterweight
Inverted Syphon Drain
Sump With Liquid Seal
Drain
Balloon Inflated
Balloon Deflated

Fig. 8. Wiggins balloon system.

Pressure Storage

It is quite evident that breathing losses can be stopped by any method which will prevent vapor from escaping through the relief vent. This may be done by storing volatile products in tanks designed to withstand the maximum vapor space pressures normally reached and setting the relief vents to operate at this pressure. Several types of pressure vessels have been developed for different classes of service. Of these, the most unusual is undoubtedly the Hortonspheroid, which has the shape of a drop of mercury resting on a flat surface. This shape is the one requiring the least amount of metal in the shell to hold a given volume of product at a stated working pressure.

Spheroids having the characteristic "drop of mercury" shape are known as

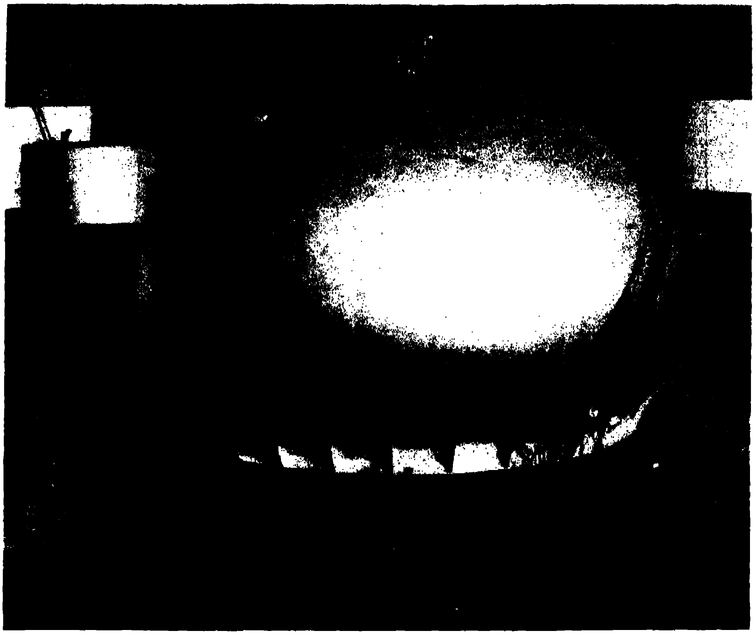

Fig. 9. 25,000-barrel 15-pound Hortonspheroid.

"smooth" spheroids because they contain no internal framing of any sort. They are built in capacities up to 40,000 bbls and for working pressures as high as 30 lbs per sq in gage. A typical "smooth" spheroid is shown in Fig. 9. In capaci-

Fig. 10. 100,000-barrel noded-type Hortonspheroid.

ties above 40,000 bbls, the spheroid is flattened out to limit the height and prevent excessive soil pressure in the foundation. This is done by constructing the roof and bottom in the form of series of nodes. The cusps on intersections of the roof nodes are connected with those in the bottom by circles of tension members having sufficient strength to maintain the vessel in its flattened shape under the working gas pressure. A 100,000-bbl, 10-lb Hortonspheroid of the noded type is shown in Fig. 10.

More Volatile Products

All the foregoing discussion has dealt with breathing losses from products whose boiling point is never reached at normal tank storage temperatures. Another and more serious type of standing loss occurs when the surface or any other part of the stored liquid reaches the boiling point, that is, the temperature at which the vapor pressure of the liquid is equal to the external pressure acting upon it. When this point is reached vaporization takes place at a rate depending upon the amount of heat being absorbed by the liquid. Losses of this sort may be enormous. Pressure storage usually affords the most economical means of eliminating boiling losses.

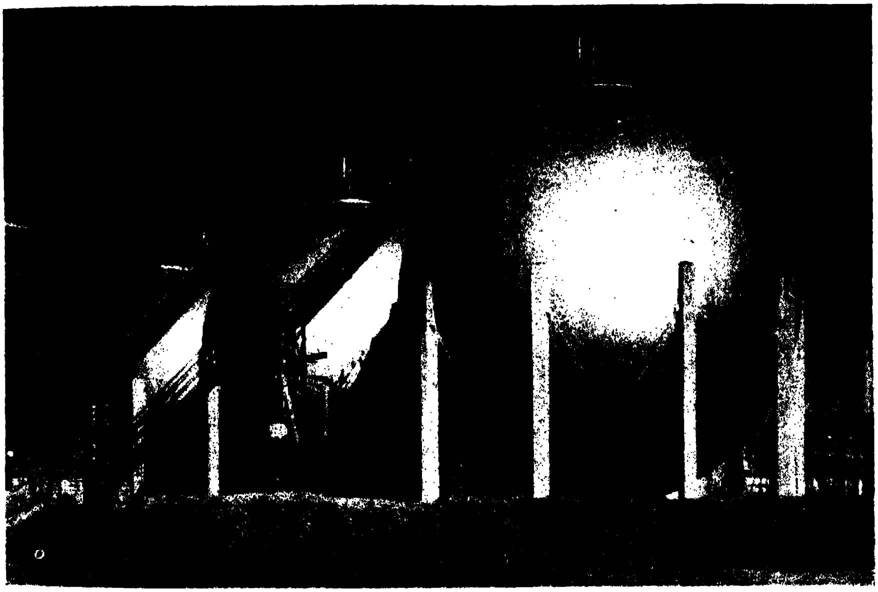

FIG. 11. Three 12,500-barrel 50-pound Hortonspheres.

Products such as the more commonly used grades of natural gasoline which require storage pressures ranging from 2½ to 30 lbs per sq in gage are normally stored in Hortonspheroids. Containers having the shape of a true sphere are better suited to hydrocarbons with higher vapor pressures, such as butanes and propanes. Hortonspheres for this class of service have been built for working pressures as high as 250 lbs per sq in. A typical Hortonsphere installation containing three units each having a capacity of 12,500 bbls and designed for a working pressure of 50 lbs per sq in is shown in Fig. 11.

Conclusion

In selecting the type of storage equipment best adapted to a given installation it is necessary to have a thorough knowledge of the probable operating conditions, including the nature of the products to be stored, their value, volume of storage required, annual throughput and the probable temperature variations in the liquid, the liquid surface and the vapor space. In a paper of this length, it has been out of the question to attempt to present an analysis of all the problems involved in the design and selection of suitable storage facilities. It is hoped, however, that the discussion herein has presented a fairly clear picture of the steps that are being taken by many oil companies to reduce temperature losses from all grades of volatile products. It is singular that the trend in evaporation loss reduction has been toward the use of devices that counteract the effects of temperature change but make no specific attempt to reduce the magnitude of the change itself.

Chapter 12

Optical and Radiation Pyrometry

Optical Pyrometry

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An optical pyrometer is a device for measuring the temperature of a hot body from a determination of either the brightness or the color of the surface of the source studied, generally by eye observations. In this paper the pyrometer and pyrometric methods discussed all apply to temperature determinations from surface brightnesses.

Since the optical pyrometer is not an absolute instrument, a calibration is necessary. This necessitates a known relation between surface brightness and temperature, and of the many sources that might be used, the blackbody is selected. Thus, unless otherwise noted in what follows, the source referred to is the blackbody.

FIG. 1.* The first optical pyrometer.

Brightness measurements cannot be made accurately by the unaided eye. However, the eye can quite accurately match the brightness of the surface studied with that of another source which necessitates a comparison source.

There have been several methods used in the construction of optical pyrometers to introduce the comparison source. The source may be off to one side and reflected into the line of sight either by a mirror or by a cube, as shown in Fig. 2, or it may be built into direct line of sight, as shown in Fig. 3, which is a diagram of the disappearing-filament type of optical pyrometer. There are also several methods by which the brightness of the comparison source can be varied so that it can be matched with that of the source being studied. Among these may be mentioned an iris diaphragm between the comparison source and the observing cube, or between the source being studied and the cube with the opening varied to bring the images of the two sources to a brightness match. The light from the source being studied and the comparison source may be polarized in planes at right angles to each other, and their brightnesses balanced by rotating a Nicol prism in the eye-piece. A variable absorbing screen, properly located, may be used for obtaining a balance; or finally one may follow the principle used in the disappearing-filament optical pyrometer and vary the current through the pyrometer filament to balance it in brightness with the image of the source studied.

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* Illustrations for this paper supplied through the courtesy of the *Journal of Applied Physics*.

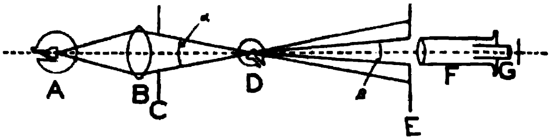

Fig. 2. Arrangement used in one form of Le Chatelier optical pyrometer.

The disappearing-filament optical pyrometer is quite similar to a telescope, the main difference being that the pyrometer filament is located at the focus of the objective lens in place of cross-hairs. In series with the lamp filament is the battery, resistance and a meter for controlling and measuring the current. Besides its simplicity of construction and use, this pyrometer has two outstanding advantages. In the first place, one can see the object whose temperature is being measured and can thus be sure just what part is being measured. Also, the temperature of objects which, because of their size or their location, would be difficult to measure by any other means can be easily measured with this pyrometer.

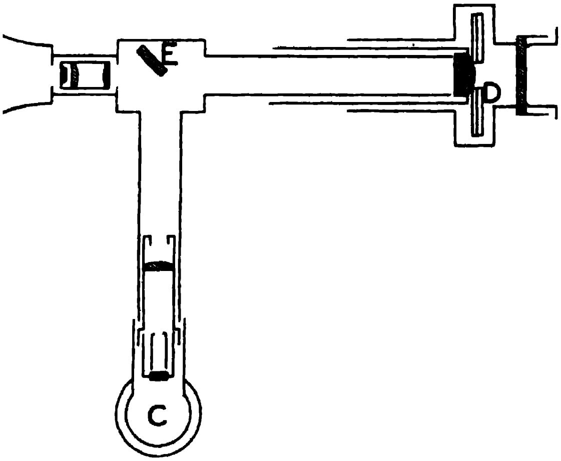

Fig. 3. Schematic arrangement of the disappearing-filament optical pyrometer.

The Optical Pyrometer as a Telescope

Since this type of pyrometer is a telescope, the ordinary precautions concerning the apparent brightness of an image observed through the telescope must be observed.[1] It seems best to have a limiting diaphragm somewhere in the eye-piece rather than to depend upon the eye as the limiting diaphragm. This one limiting diaphragm is sufficient to insure that the brightness of an object observed through the pyrometer does not vary with its distance or magnification as long as this diaphragm is filled with light. However, due to diffraction and reflection at the pyrometer filament and variation from Lambert's Cosine Law[2] of the intensity of the radiation across a round tungsten filament, the measured temperature of a source may vary with the magnification, unless there is a limiting diaphragm between the objective lens and the pyrometer filament. Two papers[3] have been published which deal with the diameter of the pyrometer filament and the relative size of the two cones of light, determined by these two diaphragms, for the best conditions of disappearance of the pyrometer filament. This will not be gone into here, but if the reader is interested, the original papers should be consulted.

The Pyrometer Lamp

The pyrometer lamp should have a very clear glass bulb and, for the most accurate work, should have plane glass windows on both sides. These windows should not be perpendicular to the axis of the telescope, but should be mounted at any angle of about 15 to 20° from the perpendicular, so as to avoid reflecting images of the filament into the field of view (Fig. 4).

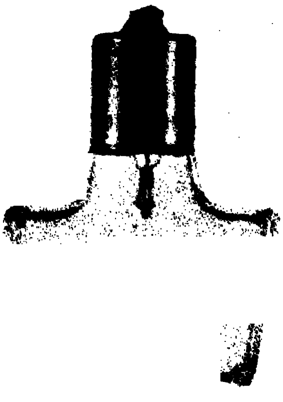

FIG. 4.
Pyrometer lamp.

A tungsten wire makes a very satisfactory pyrometer filament from the standpoint of size, operation, life, and the amount of current required. Such a pyrometer filament, if not used at a temperature higher than that of the melting point of palladium (1828 °K), will last almost indefinitely, and any failure will probably be due to accident rather than to any deterioration in the filament.

The vacuum in the bulb should be as good as one can obtain by using mercury-vapor pumps, liquid-air traps and high-temperature bake-out of the lamp and lighting the filament. A pointer or a small bend in the filament can be used to indicate the exact part used. The filament should be long enough so that the end losses from the two ends will not overlap too much, because if they do, the current-temperature relation of the filament may depend upon the ambient temperature for low filament temperatures, that is, for temperatures below 700-800 °C. A filament 3 cm or more in length will be satisfactory, except for very low filament temperatures, over a wide range of ambient temperatures. A vacuum tungsten lamp will not initially overshoot in brightness for a constant current, nor in an actual pyrometer circuit unless too much of the resistance is in the lamp leads.

Thus operated, a filament about 3 cm long and 1 to 2 mils in diameter will be within 1° of its maximum temperature in much less than one second (for temperatures above 800 °C) ; and, if it is already incandescent, it should approximate its final temperature in a shorter time.

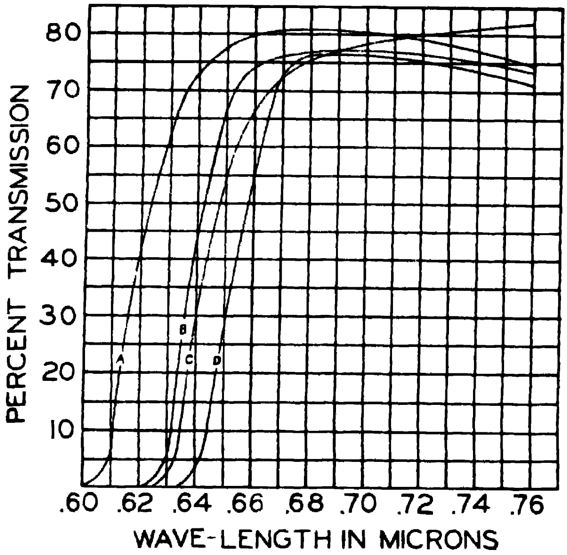

FIG. 5. Spectral transmission of various red glasses. Curve *A*—for Corning high transmission red, marked 150 per cent, five mm thick. Curve *B*—for Corning high transmission red, marked 50 per cent, 5 mm thick. Curve *C*—for Jena red 4512, 2.93 mm thick. Curve *D*—for Corning high transmission red, marked 28 per cent, 6 mm. thick.

How accurately the current through the pyrometer filament must be measured is shown by the following. If the current through the filament is of the order of .3 ampere, a change of .001 ampere corresponds to a temperature change of about 3 °C. Thus, for an accuracy of 1 °C, the current will have to be measured to about one part in a thousand. This will, in general, require some sort of potentiometer device for measuring the current.

Monochromatic Screen

Temperatures can be measured with an optical pyrometer using the total visible spectrum, but if this is done, errors are likely to be introduced and observers may differ widely in their readings in the event of a color difference between the comparison source and the source studied. This difficulty can be overcome and a much more accurate brightness match made by using a so-called monochromatic screen in the eye-piece of the pyrometer.

In general, a red glass is used as the monochromatic screen, because in the first place better red glass screens can be obtained than for other parts of the spectrum and the color change per wave-length interval is less in this part of the spectrum than in any other. When an attempt is made to extend the temperature scale, a rotating sector or an absorbing glass of higher transmission for red than for green or blue radiation can be used, which, of course, is an advantage. Also, heated objects first radiate in the red part of the visible spectrum, and thus temperature measurements can be made for a lower temperature with a red screen than with a green or blue screen.

An optical pyrometer can be so calibrated and so used that it is not necessary to know the color characteristics of the monochromatic screen. This requires a standard source for calibration that has the same brightness temperature range as the pyrometer. Also, if the pyrometer calibrated against a blackbody is used to measure the temperature of non-blackbodies, something must be known about the color characteristics of the screen. A monochromator may be used as the eyepiece of an optical pyrometer and thus a very definite wave-length may be used. This is what has been called a spectro-pyrometer.[4] However, this is not necessary unless, for some other reason, one wants to use a variety of wave-lengths. Using a good monochromatic screen and what has been defined as its effective wave-length,[5] just as definite results can be obtained as with the best monochromator; yet the instrument is not so complicated and it transmits more light. Also, such results can easily be reduced to a single wave-length if necessary.[6]

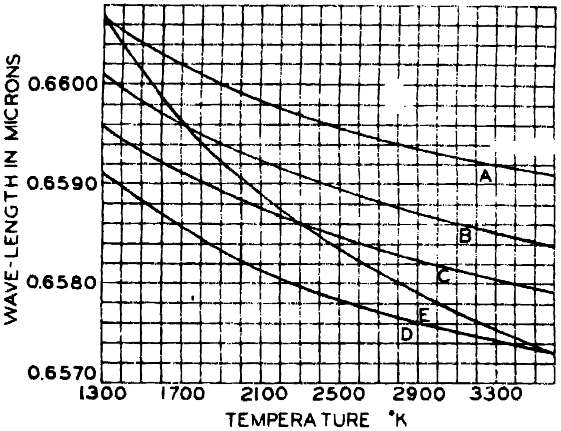

FIG. 6. Effective wave-lengths for Corning red glass. Spectral transmission shown by Curve *B*, Fig. 5. Curve *A*: effective wave-lengths from 1300° to other temperatures. Curve *B*: effective wave-lengths from 1800° to other temperatures. Curve *C*: effective wave-lengths from 2400° to other temperatures. Curve *D*: effective wave-lengths from 3600° to other temperatures. Curve *E*: limiting effective wave-length.

The effective wave-length of a monochromatic screen for a definite temperature interval has been defined as the wave-length for which the relative brightness, as calculated from Wien's equation for this temperature interval, is the same as the ratio of the integral luminosities for these two temperatures, as measured through the red screen. Expressed in the form of an equation, the following is the definition of the effective wave-length:

$$\frac{\int_0^\infty J(\lambda T_1)t_R K_\lambda d\lambda}{\int_0^\infty J(\lambda T_2)t_R K_\lambda d\lambda} \quad \left[\frac{J(\lambda T_1)}{J(\lambda T_2)}\right]_{\lambda_e} \qquad (1)$$

where $J(\lambda T)$ is the spectral distribution of the blackbody (Wien's equation), t_R the spectral transmission of the monochromatic screen; K_λ the luminosity factor, and λ_e the effective wave-length.

From this equation the effective wave-length can be calculated using Wien's equation for the energy distribution and the measured transmission of the screen for t_R. The step-by-step integration is sufficiently accurate for this purpose.

Such calculations have been made for a series of temperatures for a selected Corning selenium red glass with the transmission shown by curve *B*, Fig. 5, and the resulting effective wave-length plotted in Fig. 6.

The limiting effective wave-length[7] is the value the effective wave-length approaches as the two temperatures approach each other. The effective wave-length for a definite temperature interval is given quite accurately by the mean of the limiting effective wave-length for the two temperatures. Methods have been outlined for obtaining[8] the effective wave-length of an unknown glass by comparison with a standard glass.

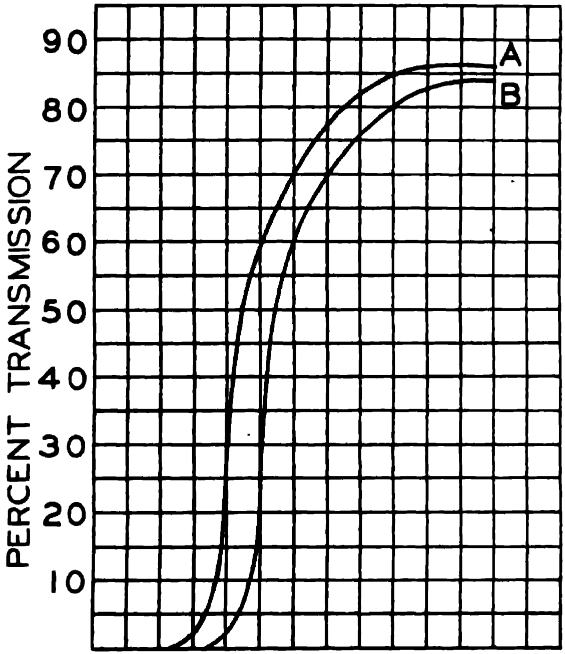

FIG. 7. Spectral transmission of a single thickness of glass *F*-4512; *A* at 20 °C; *B* at 80 °C.

The transmission of the red glass screen depends upon its temperature.[9] The curves in Fig. 7 show the transmission of one type of red screen at two temperatures. It has been shown[10] that the temperature change of transmission of this red glass will cause no appreciable error for any temperature change that is likely to occur in practice.

Rotating Sectors

It is sometimes necessary to reduce the apparent brightness of a source being studied, either for calibration purposes or to measure the temperature of a source that is higher than the pyrometer comparison source can be operated. For work in the laboratory, a rotating sector is very satisfactory for this purpose.

Position of Rotating Sector. If a rotating sector is used with a disappearing-filament optical pyrometer to reduce the apparent intensity of the background, care must be taken as to its location.[11] If the sector is placed near the lens, the image of a small source, or the edges of a large source, may not be clear. This is probably caused by diffraction due to using a part of the lens. This may cause a marked difference in the results of temperature measurements, depending on whether the sector is located near the objective lens or as near as possible to the pyrometer lamp. There is also a difference depending on the relative orientation of the openings in the sector and the source, providing the source is a lamp filament.

Table 1. Errors in Temperature Measurements Due to Improper Location of Sector.

	Near Lens–		–Near Pyrometer Lamp	
Position of 2° Sector	Opening of Sector Parallel to Background Filament	Opening of Sector Perpendicular to Background Filament	Opening of Sector Parallel to Background Filament	Opening of Sector Perpendicular to Background Filament
Current, in amp through pyrometer filament for brightness match	0.3332	0.3354	0.3357	0.3357
Apparent relative brightness	0.9390	0.9950	1.0000	1.0000
Temperature of background for these readings (°K)	2263	2275	2277	2277

In Table 1 are given results of a test showing the effect of the position of the sector. A 15-mil (0.381-mm) tungsten lamp operated at a brightness temperature of about 2275 °K was used as a background, and readings were made on the current through a 2½-mil tungsten pyrometer filament, for an apparent brightness match with a sector having two 1° openings. From the table it can be seen that the position of a sector of this size can cause an error of about 14 °K for this condition if care is not taken as to its location. When a sector is used, it should be rotated so fast that no flicker is noticeable. Not only is an error likely to be made if the sector is not rotating fast enough, but the flicker is bothersome in making accurate brightness comparisons.

Absorbing Screens

A rotating sector is not an easily portable instrument and thus is not altogether satisfactory for commercial work, that is, work that requires that the pyrometer be frequently moved about. In such cases one must use some sort of absorbing screen.

Neutral Absorbing Screens. Unfortunately it is not easy to get an absorbing screen that is of neutral tint, that is, one that has the same transmission for all parts of the spectrum. Absorbing screens that are not neutral tint have a total transmission that depends upon the distribution of energy from the source studied. The transmission for different conditions can be measured by comparison with sectored disks. This is sometimes very difficult since it is necessary to have a source with known distribution. For this a calibrated tungsten lamp can be used, the distribution being obtained from the color temperature*. A more convenient method is to measure the spectral transmission of the screen and then calculate the total transmission for the different temperatures of the source (*i.e.*, different distribution of energy) for which it is to be used. The total transmission, T_A, of an absorbing glass when used with a red glass (or any other color) is given by the following equation:

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* The color temperature of a source is the temperature necessary to operate a blackbody so that the color of its radiation will be the same as that of the source studied.

$$T_A = \frac{\int_0^\infty J(\lambda T)K_\lambda t_B t_A d\lambda}{\int_0^\infty J(\lambda T)K_\lambda t_B d\lambda} \tag{2}$$

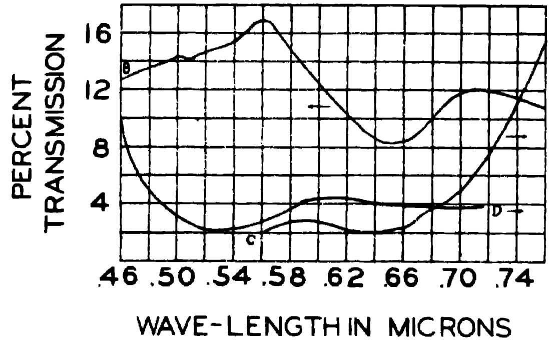

FIG. 8. Spectral transmission of various absorbing glasses. Curve B: Jena absorbing glass 1.5 mm thick. Curve C: Noviweld obtained from Corning Glass Works. Shade about 6. Curve D: Leeds & Northrup absorbing glass made of purple and green glass.

where $J(\lambda T)$ (Wien's equation) is the energy distribution, K_λ the luminosity, t_B the spectral transmission of the red glass, and t_A the spectral transmission of the absorbing glass. This integral can be calculated by the step-by-step method with sufficient accuracy for this purpose. This is done by forming the product as indicated by the equation for a number of equally spaced wave-lengths, and then taking their sum.[12]

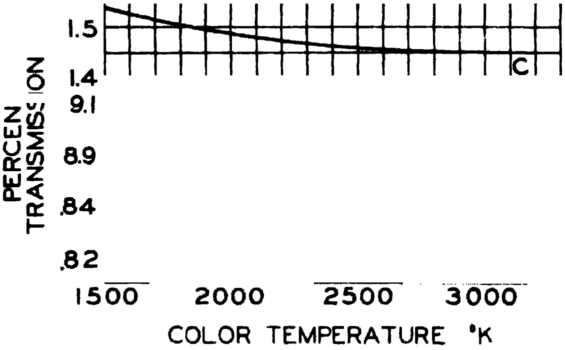

FIG. 9. Total transmission of absorbing glasses, as a function of temperature used with red glass 4512, 5.8 mm thick. Curve A: two pieces Jena absorbing glass. Curve B: one piece Jena absorbing glass. Curve C: Noviweld glass from Corning Glass Works.

In Fig. 8 is shown the spectral transmission of three absorbing screens that are suitable for this kind of work if used with the red glass whose spectral transmission is shown by curve C, Fig. 5. In Fig. 9 is shown the total transmission of two of the absorbing screens with the red screen, as a function of the temperature of the source studied. In calculating an extrapolated temperature for a particular absorbing screen, the transmission of the screen to use is the one corresponding to the temperature measured. This may require a second approximation.

The total transmission of absorbing screens may depend upon the temperature of the screens themselves. In Table 2 are given the total transmissions for two different temperatures of the glasses for two of the screens the spectral transmissions of which are given in Fig. 8. When absorbing screens are used, they must be mounted so that they can always be put back in exactly the same position, since the transmission is apt to be different in different parts of the screen.

Table 2. Transmission of Absorbing Glasses at Different Temperatures.

Temperature (°C)	Noviweld absorbing glass (%)	Jena absorbing glass (%)
20	1.70	8.96
102	1.55	8.90
200	1.39	8.87

It has been stated[13] that the absorbing screen should have such a spectral transmission that it will give a color match between the source studied and the pyrometer filament for the range of the monochromatic screen. If this is done, a monochromatic screen of wider spectral transmission can be used. Specifically, absorbing screens[13] have been suggested such that

$$\frac{1}{T_1} - \frac{1}{T_2} = \text{const.} \qquad \text{(see equation 4)}$$

that is, that $\log T_a$ varies in such a manner as to compensate for the variation in λ_e. This makes for simpler calculations and makes it easier to combine screens to extend the temperature scale greatly. Such refinements are possible but are not necessary. What must be used is a monochromatic screen and an absorbing glass of such spectral transmissions that different observers will get practically the same reading. The sharper the cut-off on the short wave-length side and the farther toward the red end the cut-off is, the easier it is to find a neutral absorbing glass that will be satisfactory to use.

Calibration

The only radiation constant that enters into the calculations is c_2 and this comes in as a factor of the exponent in Wien's equation. It might be stated here that Wien's equation is generally used in calculations for optical pyrometers rather than the more exact form of Planck's equation because, for the range of the optical pyrometer up to about 4000 °K (where the error is about 4°), Wien's equation is sufficiently accurate and is much easier to use.

It seems that a variation in the accepted value of c_2 will always be with us. The accepted value of the constant has been slowly decreased for a number of years, and now Dr. Wensel[14] makes an analysis of all of the work done on this constant and points out that a larger value is indicated. Before Dr. Wensel's analysis the accepted value was 14320 μ deg. Dr. Wensel concludes that this constant should be increased to 14360 μ deg. If a temperature, T_2, is obtained from calculations using one value of c_2, it can be reduced to the new value, T_2', by the following formula

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{c'_2}{c_2}\left(\frac{1}{T_2'} - \frac{1}{T_1}\right) \qquad (3)$$

To calibrate an optical pyrometer starting from fundamentals would be a great undertaking, but fortunately this is not necessary. The fundamentals have been well worked out and standard methods are available. One method of calibrating is by direct comparison with a blackbody at a series of known temperatures. It is, in general, not easy to bring a blackbody to a number of definite temperatures, so methods have been devised to calibrate from a blackbody held at one standard temperature.[15] When a standard blackbody furnace is used for calibrating optical pyrometers, it is held at the temperature either of melting gold or of melting palladium.

The standard radiator at the standard temperature gives one point on the calibration. To obtain another point, readings are taken of the current through the pyrometer filament for an apparent brightness match with a rotating sector, or absorbing glass of known transmission, between the pyrometer lamp and the standard blackbody. This will give a measure, in terms of the pyrometer current, of a brightness that is some known fraction of that of the standard radiator at the standard temperature. If monochromatic radiation is used, it is easy to calculate the temperature, T_2, of the blackbody corresponding to this brightness, that is, to this current through the pyrometer filament, from T_1, the standard temperature, by the following formula derived from Wien's equation:

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{\lambda \cdot \log T_A}{c_2 \log e} \tag{4}$$

where T_A is the transmission of the sector, or absorbing glass, and λ is the wavelength used. If the measurements are made with a red glass in the eye-piece, the temperature that would correspond to this fraction of the brightness of the standard blackbody can be calculated just as before, except that in this case the effective wave-length of the red glass for the temperature interval is to be used. By using a number of sectors or absorbing glasses with different transmissions, points can be obtained for a curve showing the relation between the temperature and current. In column 3 of Table 3 are given a number of apparent temperatures, each of which corresponds to the red brightness obtained when a rotating sector having the transmission given in column 1 is used between the pyrometer filament and a blackbody at the temperature of melting palladium.

Table 3. Temperatures Corresponding to Different Percentages of the Radiation from a Blackbody Held at the Temperature of Melting Palladium (1829 °K) using a Red Glass with an Effective Wave-length which Varies as is shown in Column Two. ($c_2 = 14320$ μ deg.)

Transmission of Sector	λ_e	T_2 (°K)
0.749	0.6654	1786
.499	.6655	1728
.2443	.6656	1632
.0830	.6658	1509
.0336	.6660	1426
.01668	.6662	1356
.00542	.6665	1267

The filament of the pyrometer lamp should not be heated to too high a temperature if it is to hold its calibration for any length of time. A safe temperature for a tungsten filament is somewhere in the neighborhood of 2000 °K. Since it is often necessary to measure temperatures much higher than this, some means must be provided for this purpose.

Extending Temperature Scale. If a rotating sector or an absorbing glass of known transmission is used between the source being investigated and a calibrated pyrometer lamp, its apparent brightness will be reduced and temperatures higher than the calibration of the pyrometer filament can be measured. In this case, the temperature is to be calculated from the temperature corresponding to the current through the pyrometer filament, and the transmission of the sector or absorbing glass used by means of Equation (4), except that in this case for T_A, the reciprocal of the transmission of the sector or absorbing screen is used, T_2 coming out greater than T_1.

Table 4. Extrapolated Temperatures, using Red Glass, for Various Sectors with Transmission as Given. ($c_2 = 14320\ \mu$ deg.)

Transmission of Sector → Initial Temp. (°K)	0.2443		0.0830		0.01664		0.00542	
	λ_e	°K	λ_e	°K	λ_e	°K	λ_e	°K
1200	0.6675μ	1303	0.6673μ	1398	0.6670μ	1555	0.6668μ	1693
1300	.6671	1421	.6668	1530	.6665	1727	.6663	1899
1400	.6667	1541	.6664	1672	.6661	1909	.6659	2119
1500	.6663	1663	.6660	1816	.6657	2100	.6654	2354
1600	.6659	1788	.6656	1964	.6652	2299	.6650	2610
1700	.6655	1913	.6652	2117	.6648	2511	.6646	2887
1800	.6651	2042	.6648	2274	.6645	2738	.6643	3185
1900	.6647	2171	.6645	2434	.6642	2967	.6640	3514

A convenient method is to work out such extrapolated temperatures for the various sectors and absorbing glasses that are to be used, and plot the extrapolated temperatures against the temperatures as determined from the pyrometer reading. Such curves can then be used with any pyrometer using the same red glass, providing the same sectors or absorbing glasses are used.

In Table 4 is given a series of such extrapolated temperatures using different sectored disks. In column 1 are given the initial temperatures; that is, the tem-

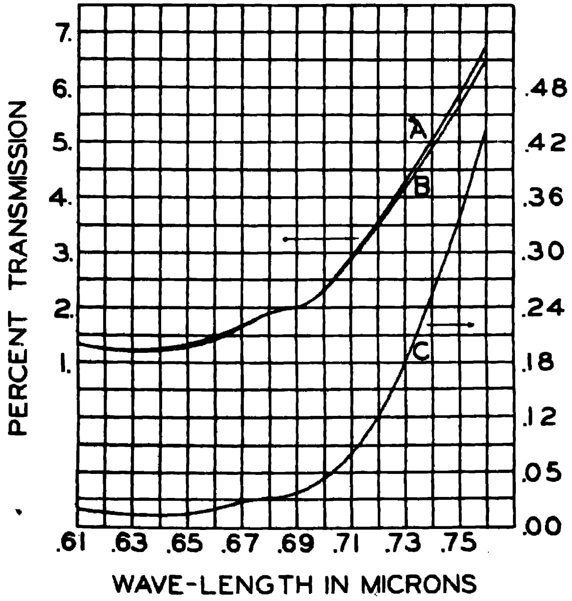

FIG. 10. Spectral transmission of two absorbing screens (Curves *A* and *B*) and the spectral transmission of the two together (Curve *C*).

peratures that would correspond to the pyrometer reading without any sector. In columns 3, 5, 7 and 9 are given the extrapolated temperatures corresponding to the same pyrometer readings when the sector, the transmission of which is given at the head of the column, is used between the pyrometer lamp and the source studied, and a red glass having the effective wave-length shown in columns 2, 4, 6 and 8 is used in the eye-piece.

In connection with some special work it was necessary to extend the calibration of an optical pyrometer to measure temperatures up to about 6000 °K. This was done by using two absorbing glasses between the pyrometer lamp and the source being investigated. The spectral transmissions of the two glasses are shown by curves *A* and *B*, Fig. 10, and that of the combination as shown by curve *C*. Since neither of these absorbing screens is of neutral tint, their combined total transmission is not the product of their individual transmissions. The combined transmission of any wave-length is, however, the product of their individual transmissions at this wave-length. Curve *C* was obtained from the product of the spectral transmissions of the two glasses at the different wave-lengths.

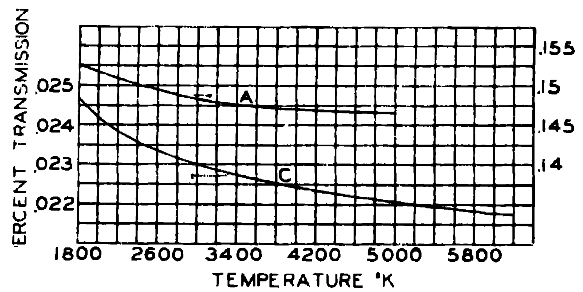

FIG. 11. Total transmission for red radiation of the absorbing screen whose spectral transmission is shown by Curve *A*, Fig. 10, and of the two absorbing glasses whose spectral transmission is shown by Curve *C*, Fig. 10.

The transmission of either of these glasses alone was readily measured, whereas a single absorbing glass with a transmission equal to that of the combination of the two would have been very difficult to measure. The total transmissions of these absorbing glasses for red radiation were calculated from their spectral transmissions by Equation (2) for various temperatures of incident radiation and are shown in Fig. 11. From the values of the total transmissions thus obtained, the extrapolated temperature for one glass and for the combination of the two were calculated by means of Equation (4) and are shown in Table 5. It will be seen that when the two glasses are used together, temperatures may be measured up to about 6000 °K.

Table 5. Extrapolated Temperatures using Red Glass for One Absorbing Glass and for Two Absorbing Glasses Having the Transmissions Shown in Figs. 8 and 9. ($c_2 = 14320 \mu$ deg.)

Initial Temp. (°K)	Transmission of one absorbing glass	Extrapolation temp. for one absorbing glass (°K)	Transmission of two absorbing glasses	Extrapolated temp. for two absorbing glasses (°K)
1200			.000238	2228
1300			.000233	2604
1400	.0149	1922	.000230	3045
1500	.0148	2115	.000227	3565
1600	.0147	2321	.000224	4143
1700	.0147	2539	.000221	4965
1800	.0146	2770	.000218	5942

Since it is not always convenient or possible to operate a blackbody for the calibration of an optical pyrometer, some substitute is necessary. A tungsten lamp with either a wire or ribbon filament can be calibrated as a standard of brightness and used for this purpose. It is sometimes convenient to have the filament calibrated so that the currents are known for the brightnesses as observed through a definite monochromatic glass for the blackbody at the temperature of melting gold and melting palladium.

It has been found that such a lamp, if not operated at a higher temperature than that necessary to give a red brightness the same as that of a blackbody at the palladium point, will have a very long life.

About twenty-six years ago two 7.5-mil hairpin-filament vacuum-tungsten lamps were calibrated in the laboratory at Nela Park as standards of the same brightness observed through our red glass, as a blackbody at the melting point of palladium. For about ten years these lamps were checked from time to time against the standard blackbody at this temperature. For the past fifteen years we have not operated our blackbody and these two lamps were our only standard of brightness corresponding to the palladium point. About two years ago Dr. Wensel of the National Bureau of Standards calibrated these lamps at the currents for a brightness corresponding to the palladium point. Dr. Wensel's calculations showed these two lamps now agreed with the National Bureau of Standards value of the brightness of a blackbody at the palladium point, for the effective wave-length used to better than 1 °C.

Such standard lamps are very valuable for a hurried check on the calibration of an optical pyrometer since they can be calibrated at several points over the range desired to calibrate the pyrometer lamp. These standard lamps can be calibrated at a much higher temperature than 1828 °K and still have a satisfactory life. It must be remembered, however, that these are supposed to be standard lamps and that this is the brightness temperature, and that the true temperature is about 150 °C higher than the brightness temperature (at 1800). Another point to keep in mind is that a tungsten lamp, pyrometer-calibration standard, must be standardized for the same effective wave-length as that of the monochromatic screen on the pyrometer where it is to be used.

Accuracy

Accuracy Tests. A number of experiments have been made that show the accuracy that might be expected in the use of the disappearing-filament type of optical pyrometer. In the first experiment, readings were made by a number of observers who had no experience in this kind of work. The instrument used was the laboratory form of pyrometer. The resistance that controls the current through the pyrometer filament was so chosen that the sliding contact had to be moved quite a distance in order to change the apparent brightness of the filament by an appreciable amount. The current was measured by means of a potentiometer.

In Table 6 are given the results of this experiment. Observers 1 and 2 were high-school graduates with several months' experience as laboratory assistants. Observer 3 was a man with several years' experience in shop work. Observer 4 was a man with several years' experience in a lamp factory. Observers 5 and 6 were girls from the lamp factory; No. 5 had no experience with this kind of work, while No. 6 had had experience with the photometer.

The table shows that but a single observer made an error greater than 3 °K in the temperature as obtained from the average of six readings. In no instance was a value of temperature obtained from a single reading that differed more than 5° from the mean of the set of readings.

Table 6. Results Obtained with the Disappearing-Filament Type of Pyrometer by Inexperienced Observers.

Observer	-Value obtained for temperature,— as an average of six readings (°K)		Variation of single readings from mean (°K)
Standards	1438	1643	
(1) L.C.	1439	1643	4
(2) H.W.	1438	1642	3
(3) F.G.	1439	1642	2
(4) E.H.	1436	1644	3
(5) E.W.	1436	1636	5
(6) L.R.	1436	1640	2

In the second experiment four experienced observers made readings with two pieces of Jena red glass No. 4512 (spectral transmission shown by curve *C*, Fig. 5) in the eye-piece of the pyrometer, on the apparent brightness of a particular source as observed first through a rotating sector with two 1° openings, secondly through the Noviweld absorbing glass having the spectral transmission shown by curve *C*, Fig. 8, and thirdly through two pieces of Jena absorbing glass having the spectral transmission shown by curve *B*, Fig. 8. The source used was a 15-mil tungsten lamp operated at a color temperature of 2610 °K. Values of the current through the pyrometer filament thus obtained are given in Table 7. The maximum range with the two glasses occurs for K. H. M. and W. E. F. for the Noviweld glass when the Jena red glass No. 4512 was used. This amounted to about 1 per cent in brightness and to less than 5° in temperature at about 2500 °K.

Table 7. Results Obtained by Experienced Observers Using Different Red Glasses and Different Absorbing Glasses.

			—Current through pyrometer filament— for apparent brightness match with		
Observer	Red glass used	Direct	2° Sector	Noviweld Absorbing Glass	Two Jena Absorbing Glasses
I.A.V.	Jena No. 4512	0.4343	0.3358	0.3804	0.3547
K.H.M.	Jena No. 4512	0.4343	0.3361	0.3807	0.3546
W.E.F.	Jena No. 4512	0.4343	0.3361	0.3803	0.3546
A.G.W.	Jena No. 4512	0.4343	0.3358	0.3805	0.3547
I.A.V.	Corning Red	·0	0.3380	0.3784	
K.H.M.	Corning Red		0.3380	0.3785	
W.E.F.	Corning Red		0.3380	0.3783	
A.G.W.	Corning Red		0.3378	0.3784	

A third experiment [16] shows, in another way, what results are to be expected with the optical pyrometer. A number of tungsten-filament lamps were calibrated at the laboratory at Nela Park for a wide range of brightness temperatures (1200-2700 °K) and sent to the National Bureau of Standards, the National Physical Laboratory of England, the Physikalisch-Technischen Reichsanstalt in Berlin, the Laboratoire Central in Paris, the General Electric Research Laboratory at Schenectady, the Physics Laboratory at the University of Wisconsin, the Laboratory of the Philips Glowlampworks in Eindhoven, and the laboratory of the Osram Lamp Company at Berlin. In some cases two lots of lamps were exchanged and the final outcome was a check that was much better than one would expect in this kind of work when one considers that in each laboratory the pyrometer was calibrated against a blackbody, the lamps operated and their temperature measured with an optical pyrometer.

Another test that shows the accuracy that can be obained with this type of pyrometer is the comparative measurements made on a carbon arc conducted by Dr.

Chaney.[17] These arcs were measured in the laboratory of the National Carbon Company, in our laboratory here at Nela Park, and in the laboratory of the National Bureau of Standards, with the results given in Table 8, which indicate an agreement better than one has a right to expect. The determination of the melting point of platinum that occurred in the establishment of the Waidner and Burgess [18] standard of light intensity can be given as another check on the accuracy obtainable. In establishing this scale, platinum was melted in a special blackbody in several standardization laboratories with the results given in Table 9. These results are the average of a number of settings, but nevertheless they indicate the high degree of accuracy that can be obtained with very special care.

Table 8. Brightness Temperature of a Special Carbon Arc as Measured in Three Laboratories.

National Carbon Co.	*3820 °K
Nela Park	*3811
National Bureau of Standards	3821

*Corrected to International Temperature Scale since data published by Dr. Chaney.

Table 9. Melting Point of Platinum as Determined in Connection with Establishment of Waidner and Burgess Standard of Light Intensity.

National Bureau of Standards	1773.5 °C
National Physical Laboratory	1773.3
Physikalisch-Technischen Reichsanstalt	1773.8

Table 10 was prepared to show what errors in the final temperatures would result from errors in certain constants or from certain other causes. The results given in this table indicate the care necessary in calibrating and operating this type of optical pyrometer to reach the standard of accuracy desired.

Table 10. Changes in Temperature of 2400 and 3000 °K Extrapolated from 1800 °K as Initial Temperature, Using Wien's Equation, Due to Various Changes.

	Percentage change			Actual change (°K)		
Variation leading to error	1800	2400	3000	1800	2400	3000
Change of 1% in initial temp.	1.0	1.30	1.70	18.0	32.0	50.0
Change of 3 °K in initial temp.				3.0	5.0	8.0
Using a wave-length 1% in error		0.30	0.70		8.0	20.0
0.001 μ error in wave-length		0.05	0.10		1.2	3.0
If the λ_e of red glass between 1300 and 1800 °K is used in extrapolating (see Fig. 6)		0.10	0.30		2.4	7.5
Calibrating pyrometer filament against tungsten lamp as background that was standardized with a red glass different from one used in pyrometer being calibrated. Suppose λ_e to change from 0.665 to 0.650 μ.				3.5		
Error of 1% in value used for transmission of sector or absorbing glass		0.26	0.32		6.2	9.6
Variation of 1% in current through 2½-mil pyrometer filament	0.5	0.70	0.80	9.0	16.0	25.0

Temperatures of Non-Blackbodies

The discussion concerning the optical pyrometer thus far applies to observations, comparisons, and computations for a blackbody. The optical pyrometer is, however, a very useful instrument for studying the radiating characteristics of non-blackbodies as well, and it has been used in many such investigations.

If proper precautions are taken, quite accurate results can be obtained with this instrument in studying non-blackbodies, *i. e.*, those which radiate less for some or all wave-length intervals than a blackbody. Most non-blackbodies can be so prepared, *i. e.*, surface conditions, that their radiation characteristics are quite constant for any definite temperature.

An optical pyrometer measures the brightness of a surface for a definite wave-length interval, and a temperature can be calculated from this brightness under the assumption that the brightness is obtained from a blackbody. Thus, if a non-blackbody has the same brightness as a blackbody at a temperature of 1500 °K, it will be said to have a brightness temperature of 1500 °K which is lower than its true temperature.

To obtain the true temperature from these brightness temperatures, one must know something about the radiating characteristics of the source studied. In this particular instance one wants to know the ratio of the brightness of the source studied to that of a blackbody for the same temperature and wave-length interval. This ratio is called the emissivity and its significance and methods of measuring it will be discussed later.* The true temperature, T, can be calculated from the brightness temperature, S_λ, and the emissivity, e_λ, by the following equation.

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda e \log e}{c_2 \log e_\lambda} \tag{5}$$

If a spectro-pyrometer is used for these measurements, the wave-length will be quite definitely determined and there will be no question concerning the wave-length used. Can this be done if a monochromatic screen is used?

The first question, of course, is the wave-length to which this brightness temperature should be ascribed. The brightness temperature, S_λ, must be ascribed to a wave-length such that the energy emitted by a blackbody per unit area at temperature T $(=S_\lambda)$, for this wave-length will equal that emitted per unit area by the source for the same wave-length. Thus, there are two sources with different spectral distributions that have the same brightness when observed through the red screen: a blackbody at temperature T $(=S_\lambda)$ and the source studied, which is at a brightness temperature S_λ. Call the color temperature of the source T_c. As these two distributions are different and yet the sources have the same brightness, the curves representing these distributions must cross if they are plotted with energy emitted per unit area against wave-length. The point at which these two curves cross evidently gives the wave-length to which the brightness temperature, S, is to be ascribed.

It can be shown [6] that the wave-length for which these two curves cross is the effective wave-length for the temperature interval between a temperature T $(=S_\lambda)$ of a blackbody and T_c, the color temperature of the source studied. This means that the different brightness temperatures of a non-blackbody will, in general, be ascribed to different wave-lengths.

Sometimes it is desirable to know the brightness temperature over quite a range of temperatures for the same wave-length. If the color temperature of the source is known, the brightness temperature can be calculated for any wave-length when it is known for one wave-length. Thus, for a source at a color temperature, T_c, using Wien's equation and the conditions that hold for color match, the following relation between two brightness temperatures (S_{λ_1} and S_{λ_2}) for two wave-lengths (λ_1 and λ_2) can be derived.

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* See paper by Worthing, later in this chapter.

$$\frac{1}{S_{\lambda_2}} = \frac{\lambda_2}{\lambda_1}\left(\frac{1}{S_{\lambda_1}} - \frac{1}{T_c}\right) + \frac{1}{T_c} \tag{6}$$

For a good red glass, this correction is small. If a double thickness (6.8 mm) of the red glass, known as Jena Rotfilter No. 4512 (spectral transmission shown by curve *C*, Fig. 5), is used before the eye-piece of the pyrometer, this correction when applied to the brightness temperature of such a metal as tungsten will be small. The effective wave-length of this red glass is 0.6657 μ, for the range between brightness and color temperature of tungsten, at a brightness temperature of 1600 °K; and for this same range for tungsten at a brightness temperature of 3000 °K, is 0.6626 μ. If the higher brightness temperature is corrected to a wave-length 0.6657 μ, the correction will amount to about −2 °K. For most work when using this screen, this correction will be negligible.

Thus, just as definite results can be obtained using an optical pyrometer with a good monochromatic screen as with a spectro-pyrometer. If one wants to study the radiating characteristics of a particular source for different parts of the spectrum, it is only necessary to obtain a monochromatic screen for that part of the spectrum.

If the effective wave-length of the red glass used is known for different temperature ranges, the results can be treated just as definitely as if an absolutely monochromatic screen were used; in addition, the red glass has the added advantage of transmitting enough light to enable very accurate brightness comparisons to be made.

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The Fluorescent Mercury-vapor Lamp as a Light Source for a Single-point Check on Optical Pyrometers

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It is often desirable to have a dependable light source for making a quick and convenient single-point check on an optical pyrometer. The 15-watt pink fluorescent mercury-vapor lamp has been studied and the results show that its characteristics make it suitable for such use.

Optical pyrometers are usually calibrated by the use of a wide-ribbon filament tungsten lamp. A set-up of this type has been described by Baeyertz and Perkins.[1] Because of initial and upkeep costs, equipment for calibrating optical pyrometers has been limited largely to specialized laboratories, users of large numbers of optical pyrometers and to centralized laboratories such as are maintained by associations or groups of small industrial plants. As a result, many users of optical pyrometers, especially those in the small industrial plants, do not have at hand a suitable light source for calibrating their instruments.

Aside from the facilities for calibration, a large number of industrial plants and other users of optical pyrometers do not have a suitable light source for making a check on their optical pyrometers. Consequently, in a number of instances, instruments have been in gross error without the user having the slightest knowledge of it. A simple check would serve, in most cases, to eliminate such errors.

A method utilizing the freezing points of killed steel ingots for checking the standardization of optical pyrometers has been described by Cook.[2]

The less expensive and more "portable" set-up for making checks rather than a calibration usually has as the light source a calibrated ordinary incandescent light bulb, or a projection lamp with suitable screens. These lamps have certain disadvantages, such as too small an area of uniform brightness, need of a rather accurate means for indicating and controlling lamp output and the dissipation of an inconvenient quantity of heat. The 15-watt pink fluorescent mercury-vapor lamp recently placed on the market is free from these drawbacks.

Fifteen pink 15-watt fluorescent mercury-vapor lamps 18 inches long and 1 inch in diameter were used in the study of the fluorescent lamp as a light source for a single-point check on optical pyrometers. The lamps designated as 18-inch T-8 pink fluorescent Mazda lamps were obtained from the Fluorescent Lamp Works of the General Electric Company at Cleveland, Ohio. The lamps were selected after a seasoning period of 100 hours as having approximately the same voltage drop and the same brightness as given by eye observation. A circle approximately ⅜ inch in diameter was drawn with India ink at the central region of each lamp. Observations were confined to the area within the circle. The thermal-switch type auxiliary was used with lamps in the present work. No doubt lamps of other manufacture seasoned and selected in the same manner would yield results similar to those obtained with the present lamps.

Two commercial optical pyrometers of different type and manufacture were used for making observations on the lamps. One pyrometer was of the disappearing-filament type manufactured by the Leeds and Northrup Company. This instrument was of the model previous to the potentiometer direct-reading model recently

Table 1. Initial Apparent Brightness Temperature for the 15 Lamps Observed

Line Voltage, 115 Room Temp., 86 °F.

Lamp No.	Temp.(°F)	Lamp No.	Temp.(°F)
1	2028	9	2042
2	2028	10	2038
	2023	11	2028
	2038	12	2038
	2033	13	2019
	2035	14	2040
	2020	15	2025
	2015		

placed on the market by that company. The other instrument was of the wedge type manufactured by the Pyrometer Instrument Company. Both pyrometers had red filters of approximately 0.65 μ wave-length. The apparent brightness temperatures were found to be the same, within the limit of experimental error, for both pyrometers.

The initial apparent brightness temperatures of the fifteen lamps observed are given in Table 1. The value given in the table is the average obtained from observations with both pyrometers. The two values were identical for a number of the lamps and the maximum difference for any pair was 10 °F. Lamps 8 and 9 showed the low of 2015 °F and the high of 2042 °F respectively in initial brightness temperature. The 27 °F difference between these two values is real. The existence of a difference was easily confirmed by matching the pyrometer on one lamp, then sighting the pyrometer, so adjusted, immediately on the other lamp. A very definite lack of match was observed. The variation observed in the initial brightness temperatures of the fifteen lamps indicates that unless the lamps are critically selected after a seasoning period of 100 hours each lamp should be individually calibrated for apparent brightness temperature.

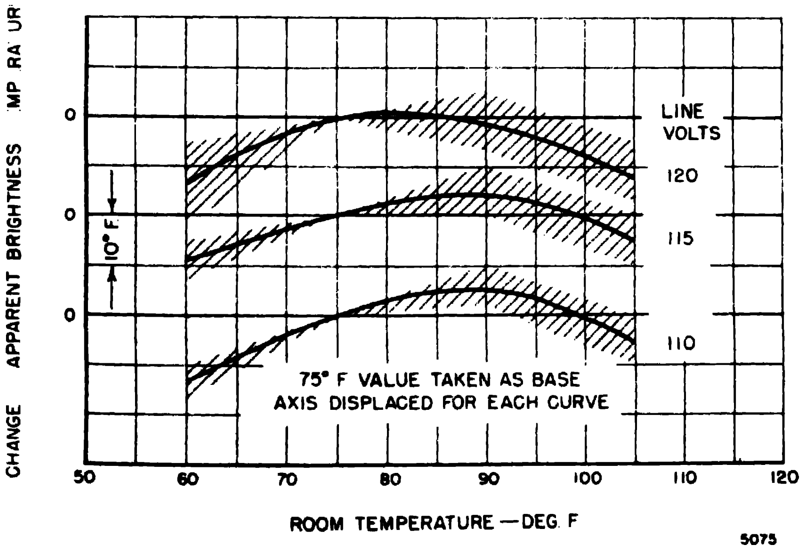

Fig. 1. The effect of room temperature for three line voltages on the apparent brightness temperature of five pink fluorescent mercury-vapor lamps.

Data in the literature by Barnes,[5] Beese,[4] Inman,[3,5,6] Marden,[4] Meister,[4] and Thayer[5,6] relative to the general characteristics of the fluorescent mercury-vapor lamp indicate that ambient temperature, line voltage, lamp current and lamp life are the principal factors to be considered in the use of the lamp for making checks on optical pyrometers.

Five of the fluorescent mercy-vapor lamps were placed in a controlled-temperature cabinet. Provision was made so that there was no intervening material, such as glass, between the lamp being observed and the optical pyrometer. Observations with the optical pyrometer were made on the lamps at various air temperatures and line voltages. The air temperature will hereafter be referred to as room temperature. Lamp current and lamp voltage were also observed.

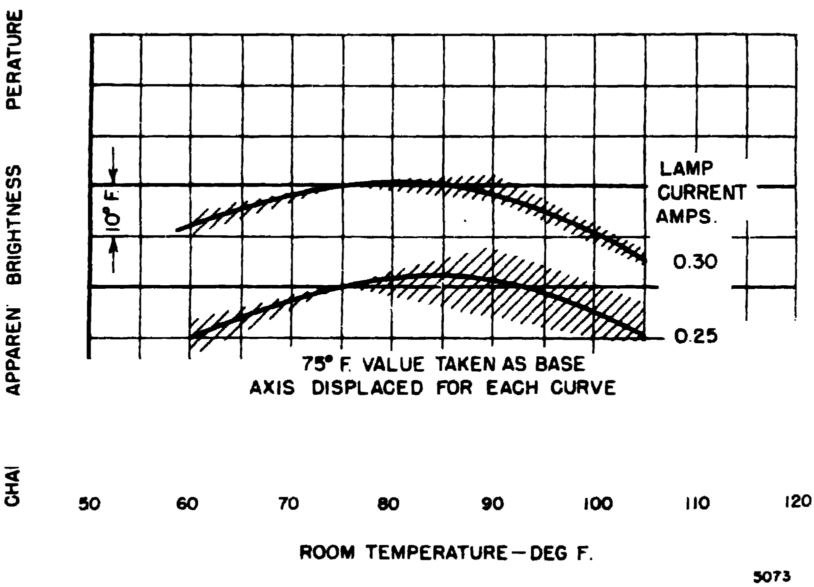

Fig. 2. The effect of room temperature for two lamp currents on the apparent brightness temperature of five pink fluorescent mercury-vapor lamps.

Fig. 1 shows the effect of variation in room temperature for three line voltages on the apparent brightness temperature of the lamps. In this and following figures the shaded area represents the spread in observed data and the solid line the average curve. Fig. 2 shows the effect of variation in room temperature for two lamp currents on the apparent brightness temperature of the lamps. In Table 2 are given

Table 2. Lamp Wall Temperatures for One Pink Fluorescent Lamp at Observed Line Voltages and Room Temperatures.

Room Temp. (°F)	—Lamp Wall Temperature (°F)— 110 Volts	115 Volts	120 Volts	125 Volts
60	88.2	90.5	94.7	—
75	102.1	104.3	108.2	110.2
90	113.7	118.6	121.3	—
105	129.4	131.3	134.8	136.3

Min. lamp wall Temp., 88.2 °F = (31.2 °C)
Max. lamp wall Temp., 136.3 °F = (58.0 °C)

the lamp wall temperatures at various room temperatures for one of the lamps. The variation in light intensity with lamp wall temperature has been reported for fluorescent lamps by Marden, Beese, and Meister[4] and is reproduced in Fig. 3. It will be noted from Table 2 that the range of lamp wall temperature (31 to 58 °C) resulting from room temperature of 60 to 105 °F comes in the region of maximum light intensity of Fig. 3. Since the optical pyrometer measures monochromatic intensities, the data of this figure are not directly applicable but serve to indicate that the general shape of the curves of Figs. 1 and 2 is as might be expected.

The effect of variation in line voltage and lamp current for four room temperatures on the apparent brightness temperature of the lamps is shown in Figs. 4 and 5, respectively. From Fig. 4 it will be observed that a change of approximately 15 °F in apparent brightness temperature results from a change of 5 volts in line voltage. Fig. 5 shows that approximately the same change in apparent brightness temperature results from a change of 0.05 ampere in lamp current. These data indicate that meters of only moderate accuracy are required for indicating adjustments in line voltage and lamp current to obtain with reasonable accuracy a certain apparent brightness temperature at any given room temperature. Since the line voltage measurement includes the voltage drop across the auxiliary reactance, lamp current is preferred to line voltage for use in adjusting the lamp to a given apparent brightness temperature.

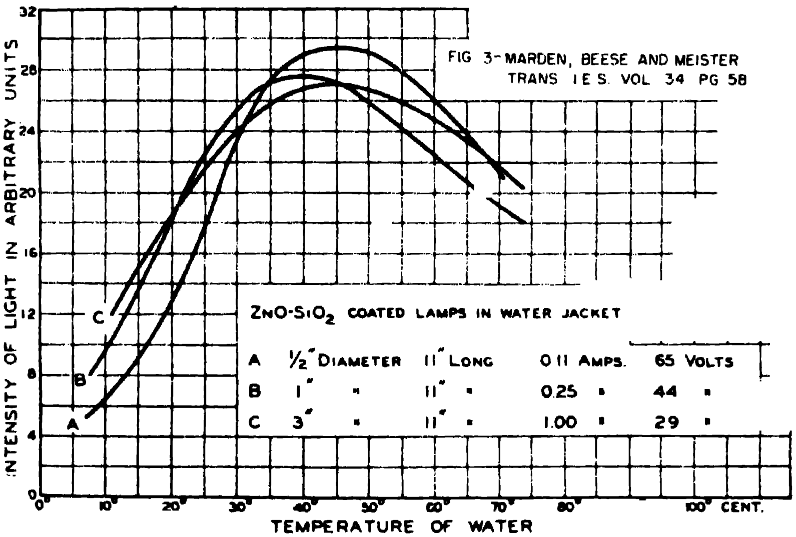

Fig. 3. The effect of temperature on light from fluorescent lamps immersed in water (Marden, Beese and Meister[4]).

Fig. 6 is a reproduction of two curves from a figure given by Inman[3] showing the characteristic changes for the fluorescent lamp with changes in line voltage. The shaded area of this figure shows the spread in the data obtained in the present investigation. The figure is presented to show that the general characteristics of the lamps used in the present work are in agreement with published data.

Ten of the pink 15-watt fluorescent mercury-vapor lamps were observed for the effect of lamp life on apparent brightness temperature. As stated previously,

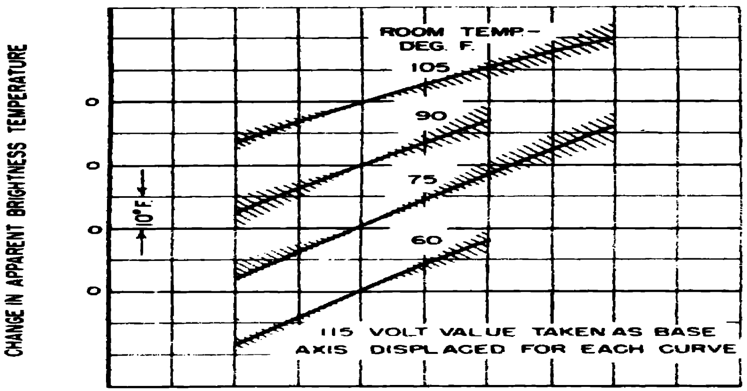

FIG. 4.

The effect of line voltage for four room temperatures on the apparen brightness temperature o five pink fluorescent mercury-vapor lamps.

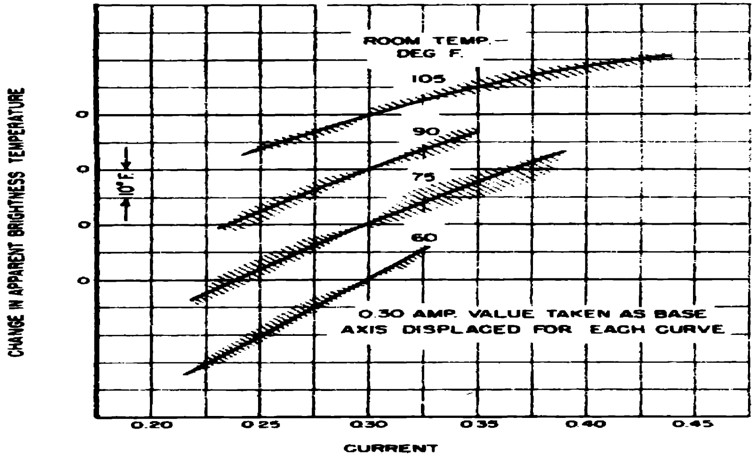

FIG. 5.

The effect of lamp cu rent for four room te peratures on the appare brightness temperature five pink fluorescent me cury-vapor lamps.

all lamps had been given a seasoning period of 100 hours; hence the times and cycles given in life tests are in addition to this period. During the life tests the lamps were operated at 115 volts line voltage, and corrections for variation in room temperature were made according to the 115-volt curve of Fig. 1. The largest correction was 6 °F, and for practical purposes it can be said that the tests were made under constant conditions.

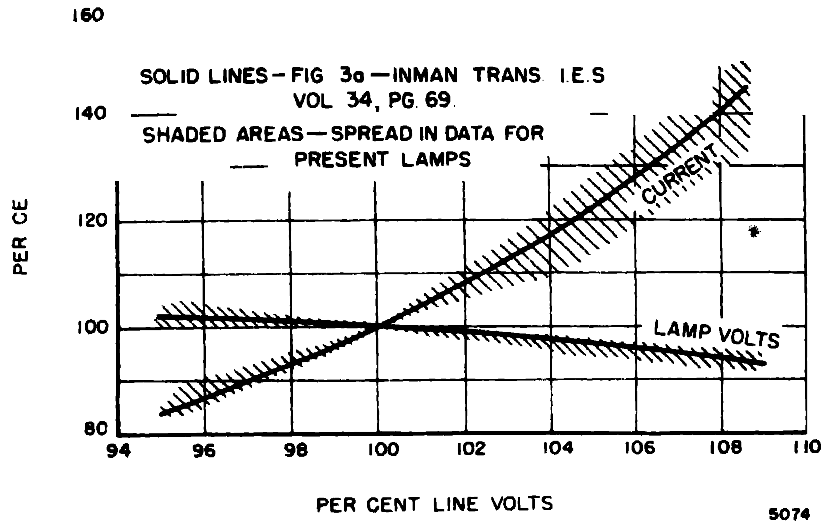

FIG. 6. Changes in lamp current and lamp voltage with variation in line voltage for fluorescent mercury-vapor lamps (115-volt value at each of four room temperatures taken as base).

Five of the life test lamps were operated continuously for 180 hours. Observations were made at 10-hour intervals. Table 3 gives the initial, maximum, minimum, and final apparent brightness temperatures observed during the tests. The greatest difference between maximum and minimum observed apparent brightness temperature for the lamps was 21 °F (lamp number 13). Since the initial and final temperatures for most of the lamps were between the maximum and minimum values observed, it is evident that, for check purposes at least, continuous operation of the lamps for 180 hours after a seasoning period of 100 hours had no effect on the apparent brightness temperature of the lamps. The differences in observed apparent brightness temperatures for a given lamp are believed due largely to the personal factor always present in optical pyrometer measurements.

Table 3. Apparent Brightness Temperatures for 180 Hours Continuous Operation.*

Lamp No.	–Temperature (°F)–			
	Initial	Maximum	Minimum	Final
11	2028	2034	2016	2020
12	2038	2039	2022	2025
13	2019	2026	2005	2013
14	2040	2039	2026	2027
15	2025	2030	2016	2022

*Lamps seasoned 100 hours before test.

The other five life test lamps were operated intermittently. A cycle of 10 minutes on and 10 minutes off was used. Table 4 gives the initial, maximum, minimum, and final observed apparent brightness temperatures for the lamps during a 540-cycle test. Observations were made every 30 cycles. The greatest variation in apparent brightness temperature for any one lamp was 22 °F noted for lamp number 6. The data are quite similar to those obtained for continuous operation of the lamps and show that 540 intermittent operations of the lamps for 10-minute periods had practically no effect on the apparent brightness temperatures of the lamps. Although the life test data show that, up to at least 180 hours continuous operation, or 540 10-minute intermittent operations, lamp life has no effect on the apparent brightness temperature of the fluorescent mercury-vapor lamp. Calibration of the lamp at intervals is suggested.

Table 4. Apparent Brightness Temperatures for Intermittent Operation. 540 Cycles, 10 Minutes On, 10 Minutes Off*

Lamp No.	Temperature (°F)			
	Initial	Maximum	Minimum	Final
6	2035	2041	2019	2019
7	2020	2030	2013	2019
8	2015	2030	2015	2022
9	2042	2051	2034	2035
10	2038	2048	2031	2032

*Lamps seasoned 100 hours before test.

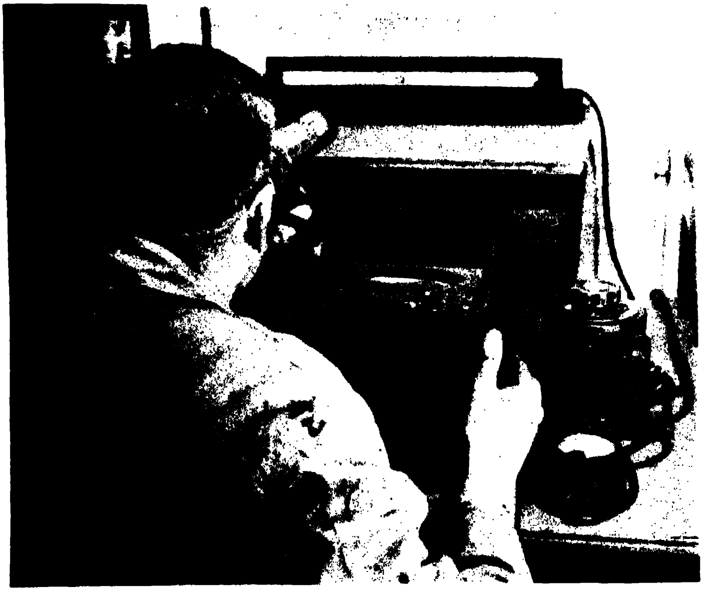

FIG. 7. Set-up for making single-point checks on optical pyrometers.

Another factor influencing the apparent brightness temperature of the fluorescent mercury-vapor lamp is the deposition of mercury at the spot being sighted on. When this occurs the mercury can be vaporized from the spot by temporarily placing thermal insulation on the tube at that location. In the observed cases this treatment has been satisfactory.

It should be observed that the fluorescent mercury-vapor lamp offers only a single-point check on the optical pyrometer and hence does not check the instrument over its entire range. In making single-point checks such things as an indicating instrument lacking uniformity in calibration, the possibility of there being spots and the like on the wedge should be taken into consideration for each optical pyrometer so checked. Suitable grey filters or sector discs could be used with the lamp to obtain a range of apparent brightness temperatures, a lower apparent brightness temperature, or, in the case of a double-range pyrometer, to give an apparent brightness temperature on the lower range such that the range filters would be the only difference between checking and use.

A set-up using the fluorescent mercury-vapor lamp for making single-point checks on optical pyrometers is shown in Fig. 7. The equipment consists of a 15-watt pink fluorescent mercury-vapor lamp, a variable auto-transformer, an indicating instrument, and a thermometer for measuring room temperature. The latter is not shown in the figure. The indicating instrument in the figure is a voltmeter connected directly across the output of the auto transformer. It is preferable, as stated, to use a milliameter measuring lamp current, and adjust current rather than voltage.

An application of the fluorescent mercury-vapor lamp of no less importance than its use in making single-point checks is in the intercomparison of two or more optical pyrometers. The observed constancy of the lamp makes it valuable for this purpose. Two optical pyrometers which check against a fluorescent mercury-vapor lamp should generally also check at other observed temperatures in subsequent use.

The simplicity, low cost, constancy and ease of control of the 15-watt pink fluorescent mercury-vapor lamp make it a suitable light source for making single-point checks and intercomparisons of optical pyrometers. The accuracy obtainable with the fluorescent lamp is as good as with lamps previously mentioned, and greater than claimed for the method described by Cook.[2] These factors suggest that optical pyrometers could be checked for gross errors at the place of use in all industrial plants. Thus the open-hearth foreman would have a means of checking and intercomparing his optical pyrometers for gross error at any time he saw fit.

Discussion

J. W. Marden, Westinghouse Lamp Division: This paper is of particular interest to the manufacturers of fluorescent lamps. It certainly is important to learn how closely these lamps checked in initial apparent brightness temperature and how little they changed with 180 hours of burning. At the time of writing this discussion only a brief description of the work was available, and with this limited information several points about the use of fluorescent lamps for optical pyrometry have occurred to us.

It is customary for the manufacturer to read the lumen output of fluorescent lamps after 100 hours burning in order to rate the lamp after the initial drop in light output has taken place. This drop is quite rapid at first, but after 100 hours burning becomes very small. It is customary with us to wait for six minutes after turning the lamp on before making a lumen reading. It is found that if temperatures are normal there is not much change after this time.

It must be borne in mind that the manufacturer of fluorescent lamps is now making no attempt to control the color value closer than is necessary to prevent objectionable appearance when lamps of different periods of manufacture are operated in adjacent positions. It is probable that the same batch and even different batches of fluorescent material made in the same factory will give lamps of similar color value, but different manufacturers may well vary the limits of tolerance to meet different requirements or to avoid customers' complaints. Two compounds have been used for the pink fluorescent coating and these may give somewhat different colors.

There are also other questions that might be brought up, such as the effect of the thickness of the coating, or perhaps different-sized lamps may not give the same color value. We should also point out that there is a considerable difference in the amount of current that various reactors made for operating these lamps will give at a definite line voltage. The regulation supplied by different transformers or chokes is not always the same, so that it might be advisable to read the current and voltage of the lamps and not of the supply line. In other words, the slopes of the curves of Fig. 4 may be different with different control devices.

If fluorescent lamps are to be used for pyrometry, the individual lamps and the operating equipment should be checked against some kind of standard for an absolute calibration point. Fortunately the "apparent brightness temperature" does not seem to be very critical to changes in current or room temperature, so that few precautions are needed.

The authors are to be congratulated on having presented such a highly instructive and useful paper.

Reply

The discussion by Dr. Marden, based on his wide experience with the fluorescent lamp, is very much appreciated by the authors. A seasoning period of 100 hours is important. It was, no doubt, largely responsible for the satisfactory results obtained in the present work. The variation in the make-up of the lamps and in the chokes used with them emphasizes the importance of calibrating each lamp before use.

The present work indicated that line voltage and apparent brightness temperature were related, at least when using the thermal-switch type auxiliary, in such a way that adjustments in temperature could be made to a good degree of accuracy with a moderately accurate voltmeter. However, on account of the possible changes in choke reactance, this method is susceptible to error and adjustment by lamp current is recommended. The change in lamp voltage for a detectable change in apparent brightness temperature is small; hence this lamp characteristic does not lend itself to the use of moderately accurate meters for adjustment of lamp temperature. In view of these facts and Dr. Marden's comment that the slopes of Fig. 4 may be different with different control devices, lamp current is definitely the characteristic to use for adjustment of lamp temperature.

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The Carbon Arc as a Radiation Standard

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It is frequently desirable in optical pyrometry to have a standard source of temperature readily available to obtain a quick check on the accuracy of the pyrometer. In the high-temperature range this need is admirably filled by a standard carbon arc. Such an arc provides a fixed temperature well above the range served by tungsten ribbon lamps, and one that does not require an accurate measurement of current or voltage to assure its reproduction. In 1935 Chaney, Hamister and Glass[1] reported an investigation on the various factors affecting the operation of such an arc, and they specified conditions under which an arc can be obtained that will give a reproducible maximum temperature of the positive crater.

For a positive electrode, the arc employs a spectroscopically pure graphite rod of ¼ inch or less diameter. Any type of negative electrode that gives a steady arc may be used, provided it contains no impurities that will emit radiation in the arc stream. A spectroscopically pure graphite rod ⅛ inch or less in diameter is recommended, or a $\frac{3}{16}$-inch carbon rod of spectroscopic purity can be used.

These are the carbons known to the trade as special spectroscopic carbons, and should not be confused with the ordinary spectroscopic carbons frequently used for less exacting work. The positive electrode is supported horizontally, while the negative is held vertically in the same plane with its tip just below the level of the positive electrode and about ¼ inch in front of it. Provision must be made, of course, for each electrode to be advanced along the direction of its axis as it is consumed in the arc. Various microscope arc lamps are available that can be adapted for burning such an arc.

The maximum current that can be forced through the arc without hissing should be provided. This is from 10 to 12½ amperes with the ¼-inch graphite positive electrode. The arc voltage will be between 60 and 70 volts. The power for this can be taken from a regular 110 volt d.c. supply line with a suitable variable ballast resistance in series with the arc. The ballast resistance is necessary to maintain arc stability. Also, the steadier the line voltage, the steadier will be the arc.

Just after the arc is started it will hiss and sputter quite a bit. However, after a few minutes have elapsed during which the graphite becomes heated, the arc will burn quietly. Then, as the current is increased, the brightly incandescent area expands until it covers the end of the electrode. Just above this current at which the arc crater is of nearly uniform brightness the arc will suddenly break out in a hissing or sputtering noise. This is accompanied by a sudden increase in current and a drop in arc voltage. The condition is called "overload," and is to be avoided. Once hissing has started, a quiet arc can be restored by temporarily decreasing the arc current, followed by a cautious increase to the optimum value. The preferred operating current is one slightly below the overload point, and is one at which the brightly incandescent region just covers the end of the electrode. The exact current at which this occurs will vary with the degree to which the electrode spindles. The amount of spindle, caused by oxidation of the graphite before it reaches the arc, will vary with different conditions of burning the arc, so that it is impossible to exactly specify the optimum current.

The relative position of the positive and negative tips also affects the steadiness of the arc. However, it is easy to determine and hold a relationship in which the face of the positive electrode burns off squarely. This can be done best by projecting an enlarged side image of the arc onto a wall by means of a simple lens. The image will show the two white-hot glowing electrodes with a violet-colored, intensely hot arc stream bridging the angle between them. The violet color of the arc stream is due entirely to cyanogen band radiation which extends intermittently over the spectral region between 3500 and 4200Å. There is no appreciable arc-stream radiation in the blue, green, or red regions of the spectrum. Consequently, pyrometric observations of the positive crater may be made through a section of the arc stream without being affected by it.

When the arc is operated under these conditions, the tip of the positive crater is maintained at the sublimation temperature of carbon. This temperature is in the neighborhood of 3990 °K, as shown later in this paper. Since carbon has an emissivity less than unity, the brightness temperature falls below the true temperature. Through the red glass of an optical pyrometer, the maximum brightness temperature of the positive crater viewed normally is 3810 °K. This measurement has an uncertainty of about 7° and is an average value arrived at from observations at three laboratories: the National Bureau of Standards; the General Electric Company, Nela Park Laboratories; and the National Carbon Company, Research Laboratories.

In arriving at the operating conditions for this arc recommended above, Chaney, Hamister and Glass conducted a great deal of research into the various factors affecting the brightness of the positive electrode of a pure-carbon arc. Since 1878 there had been discussion and controversy concerning the constancy of the brightness of the positive crater. Some investigators[2] reported a constant brightness temperature over wide ranges of current and found it to be independent of the kind of carbon used. Others[3] found a difference in the behavior of graphite and amorphous carbon and reported a difference in temperature with arc current. As an example of the variations encountered, Waidner and Burgess of the National Bureau of Standards found an 80° increase in brightness temperature when doubling the arc current, and reported that graphite gave about a 40° higher brightness temperature than amorphous carbon. On the other hand, Guckel and Kohn found that above a certain current density the brightness of the positive crater was constant and the same for all kinds of carbon. In fact, they obtained the same brightness whether the arc operated in air, nitrogen, carbon dioxide, or argon.

Chaney, Hamister and Glass assert that "in the course of a three-year search .... we succeeded in verifying every statement made on both sides of every important controversy regarding arc behavior." Arc variables were found which reduced the brightness below its maximum value. However, under the prescribed conditions of operation, the same maximum value of the crater brightness was found in both amorphous carbon and graphite. The principal factor affecting the crater brightness was found to be the current density at the active crater area. This has to be greater than a minimum value of about one ampere per mm^2 to insure the attainment of the maximum crater temperature. Chaney, Hamister and Glass found that this high current density could be reached most easily by use of small graphite positives. Thus the arc described above was concluded to be the one giving the greatest assurance of attaining the maximum brightness temperature.

Another method of obtaining a check on the temperature of the positive crater of this arc is to measure its spectral energy distribution, and to match this energy distribution against energy distribution of blackbodies at different temperatures to find the best fit. If carbon is assumed to be a greybody, that is, to have a constant spectral emissivity, the blackbody temperature that gives the best fit is the true temperature of the arc crater.

Our measurements of spectral energy distribution for this purpose were checked with the large quartz double monochromator at the Nela Park Laboratory of the General Electric Company, through the courtesy of Dr. W. E. Forsythe and Dr. B. T. Barnes. In taking these measurements, a diaphragm with a small hole (2.5 mm in diameter) was placed about 4 cm in front of the arc, so that the radiation measured was limited to that from the active crater area. The energy distribution obtained for the ¼" graphite arc is shown in Fig. 1. The three sharp peaks are due to the cyanogen radiation from the arc stream. However, the rest of the curve, except for a carbon line at 2478Å and some general arc stream radiation below 2400Å, is due to the continuous spectrum of the carbon crater. Using the portion of the energy distribution curve in the visible region of the spectrum, the color temperature was calculated. This was done by the selected ordinate method[4] and found to be 3990 °K.

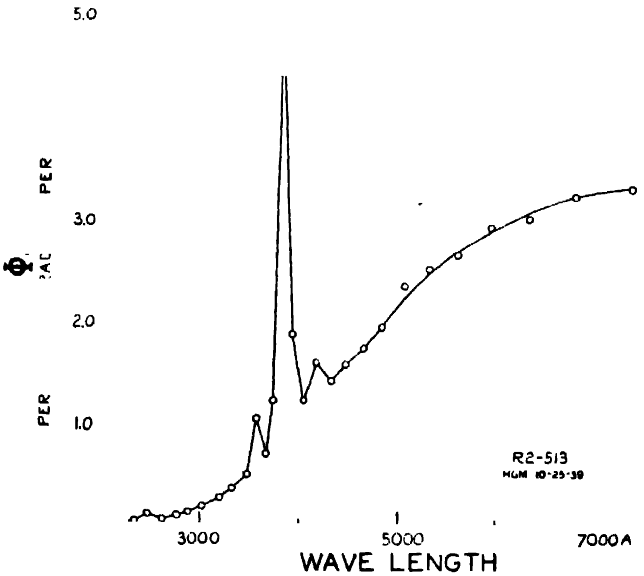

Fig. 1.

For matching the energy distribution obtained with that of a blackbody using all wave-lengths regardless of their visibility, it is convenient to plot the energy distribution in another form. Wien's law for the energy distribution of a non-blackbody is

$$\Phi_\lambda = A\epsilon_\lambda c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}} \tag{1}$$

In this equation, Φ_λ is the spectral radiant intensity; A is the area of source; $\epsilon\lambda$ is the spectral emissivity, c_1 is a constant equal to 1.177 × 10^{-12} watt/cm^2; λ is the wave-length in cm, c_2 is a second constant equal to 1.432 cm degrees; and T is the temperature. By a simple transformation this equation takes the form:

$$\log\left(\Phi_\lambda \lambda^5\right) = \log\left(A \epsilon_\lambda c_1\right) - \frac{0.6219}{T}\left(\frac{1}{\lambda}\right) \tag{2}$$

This equation is that of a straight line between the variables log $(\Phi_\lambda \lambda^5)$ and $\left(\frac{1}{\lambda}\right)$ for a greybody, *i.e.*, one of constant spectral emissivity. Consequently if we plot the energy distribution for our arc in this form, that is, plot the logarithm of the product of the intensity by the 5th power of the wave-length against the reciprocal of the wave-length, we can expect a straight line if the radiation is similar to that of a blackbody. Furthermore, the slope of this straight line will be $-0.6219/T$, so that the temperature of the arc crater can be determined from the slope of the line.

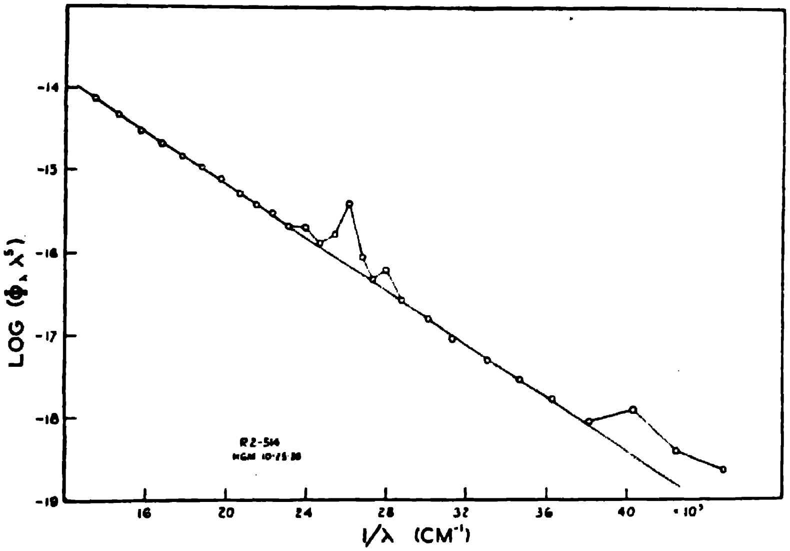

FIG. 2.

Fig. 2 shows the curve obtained for the arc with the ¼″ graphite positive when the plot is made in this way. The points fit a straight line very well, except in the region occupied by the cyanogen bands and in the region below 2500A where the arc-stream radiation becomes a contributing factor. The fact that the data fit a straight line lends added support to the assumption that the spectral emissivity of carbon is constant over this range of wave-lengths. The slope of the straight line determined by the data corresponds to a temperature of 3860 °K. We will call this temperature a "distribution temperature." It may be taken to be the true average temperature of the portion of the positive crater effective in irradiating the monochromator.

Equation (2) reveals also that the intercept of the straight line on the axis $1/\lambda = 0$ may be used to determine the emissivity of the carbon. The emissivity determined in this way is 0.91. However, the absolute magnitude of the energy ordinates is not known with as great a surety for this arc as for another arc to be described below, so that too much weight should not be attached to this particular value of the emissivity.

Another value for the emissivity can be obtained by measuring the total radiation energy of the arc. The ratio of the total energy found to that expected from a blackbody at the temperature of the arc is the total emissivity of the carbon. Since carbon is assumed to be a greybody this is also the spectral emissivity. The total energy radiated to one side of a blackbody is, by the Stefan-Boltzmann law,

$$\Phi = \sigma A T^4 \tag{3}$$

where Φ is the energy in watts, A and T are the area and temperature of the blackbody, and σ is the Stefan-Boltzmann constant, equal to 5.735×10^{-12} watt/cm^2 degree^4. The energy emitted by the arc crater in a direction normal to its surface was measured by a calibrated thermopile. This energy was then corrected by subtracting an appropriate amount for the cyanogen band radiation. The ratio of this measured energy to that calculated from Equation (3) using a temperature of 3860° for the arc crater was determined as the emissivity. The emissivity calculated in this way is 0.77. A determination of the emissivity of carbon on another arc reported later gives an emissivity of 0.78. Consequently we can take the true emissivity of carbon at the arc temperature to be about 0.775.

With the emissivity of carbon determined in this way, the true maximum temperature of the positive crater can be determined from pyrometric observations on the brightest portion of the crater. According to Chaney, Hamister and Glass, the brightness temperature of the brightest portion of the crater is 3810 °K for the wave-length 6530Å. The true temperature is determined from this by the relation

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda \log \epsilon_\lambda}{0.4343\, c_2} \tag{4}$$

where T is the true temperature, S_λ the brightness temperature, and ϵ_λ the spectral emissivity for the wave-length λ. Using an emissivity of 0.775 and a brightness temperature at 6530Å of 3810 °K, the true maximum temperature of the positive crater is calculated to be 3985 °K.

Several different temperature measurements have been reported here, and in order to avoid confusion, they will be reviewed and their relationships discussed.

(1) In the first place there is the distribution temperature, a temperature based on the relative spectral distribution of energy from a diaphragmed area of the positive crater. This temperature is calculated from Wien's law considering only the distribution and not the absolute magnitude of the energy. It is the true average temperature of the area of the crater used, provided only that the carbon is assumed to be strictly a greybody.

(2) The color temperature refers to the visual color effect of the radiation from this area of the crater. It, too, depends on the energy distribution for its calculation, but it includes only the visible radiation. Within accidental errors it would be the same as the distribution temperature if it were not for the fact that the cyanogen band radiation from the arc stream is included in its calculation.

(3) The brightness temperature is based on an optical measurement of the absolute magnitude of the radiation per unit area emitted at a wave-length of 6530Å. It is the temperature a blackbody would have if it gave off the same radiant energy per unit area at that wave-length. It applies to the brightest portion of the crater, since that is what one sights on, and is lower than the true temperature of the crater by an amount dependent upon the emissivity of carbon at the arc temperature.

(4) The true maximum temperature of the positive crater is determined from the brightness temperature by use of a numerical value for the emissivity of carbon at this temperature. This temperature and the brightness temperature refer to the

brightest portion of the crater, while the distribution temperature and color temperature are necessarily average values over an extended area of the crater. The various temperatures and emissivities have been collected in the following table.

	Standard Pyrometric Arc ¼" Graphite Positive	$\frac{5}{16}$" Carbon Positive
Distribution temperature	3860 °K	3840 °K
Color temperature	3990 °K	3855 °K
Brightness temperature	3810 °K	3670 °K
Maximum true temperature	3985 °K	3835 °K
Emissivity from intercept as in Fig. 2	*0.91	0.84
Emissivity from total energy measurement	0.77	0.78

*Data uncertain

Included in this table are values for another arc besides the standard pyrometric arc. This arc had the same arrangement of electrodes, but had a $\frac{5}{16}$" spectroscopically pure carbon positive at 12.5 amperes in place of the ¼" graphite positive. The carbon electrode is made from a lampblack base and consequently has a lower heat conductivity than the graphite. For this reason it forms a more steady arc when larger-sized positives are used than does graphite. The larger size of this carbon allowed us to use a 0.15" diameter crater shield in place of the 0.10" crater shield used for the ¼" positive, so that greater energy is available from this arc.

It will be noticed from the table that the temperatures for this arc are lower than for the standard pyrometric arc, indicating that the current density is not high enough to give the true sublimation temperature of carbon. Consequently it cannot replace the standard pyrometric arc in its use as a standard for optical pyrometry. However, there are many uses for such a steady arc as this. It can provide a source of constant brightness for spectrographic work, or it can be used as a light source for determination of high flame temperatures by the spectrum line reversal method.

Discussion

H. T. Wensel: There is very little doubt that the carbon arc operated as described by Dr. MacPherson between carbons of high purity is a remarkably constant and reproducible source and that it provides a reliable fixed point for the calibration of optical pyrometers. An accurate value of the apparent temperature of the positive crater is therefore of especial interest, but in considering the data on this temperature it is necessary to reduce all values to a common basis if a true picture of the situation is to be presented.

It has been frequently[5] pointed out that the result of an optical pyrometer measurement yields, directly or indirectly, a value of the product $\lambda \ln R$, where R is the ratio of the brightness at wave-length λ of the source in question to the brightness of some reference source. Selecting a value for the temperature of the reference source and for the constant c_2, the result is conveniently expressed on the basis of Wien's law as a single number or temperature, either t or $t + 273 = T$, by means of the equation

$$\frac{1}{t+273} = \frac{1}{t_0+273} - \frac{\lambda \ln R}{c_2} \qquad (1)$$

If the reference temperature, t_0, is the gold point with an assigned value of 1063 °C and if c_2 is assigned the value 1.432 cm deg, t will be on the International

Temperature Scale (I.T.S.). If the reference temperature is the palladium point with assigned values of 1829 °K for $t° + 273$ and 1.433 cm deg for c_2, $T(=t+273)$ will be on the General Electric Co.'s Scale[2] (G.E.S.), which was used until March, 1937, when this scale was abandoned[7] in favor of the I.T.S. As far as we know, these are the only two optical pyrometer scales that have been used since 1927, although more than a dozen such scales were used at various times before that. Each of these scales was used because, at the time, it was thought to be the best approximation to the Kelvin (Thermodynamic) Scale (K.S.). These scales when clearly defined, are all perfectly definite but are arbitrary in that the constants are arbitrarily assigned. Therefore a result can be expressed on one of these arbitrary scales such as the I.T.S. with far less uncertainty than on the K.S. The uncertainty of a value expressed on the latter scale must include the amount by which the two scales may be at variance. At the gold point the International and Kelvin Scales are probably the same within 1°, while at 3800 °K the difference[8] may be as much as 35°.

Chaney, Hamister and Glass[9] state that their result on the carbon arc is higher than that of Waidner and Burgess.[10] Actually it is lower. Waidner and Burgess expressed their result on the basis of Wien's law, 1064 °C for the gold point, and 1.45 cm deg for c_2. They substituted the results of their measurements of R at $\lambda = 65 \times 10^{-6}$ cm in Equation (2).

$$\frac{1}{T} = \frac{1}{1337} - \frac{65 \times 10^{-6} \ln R}{1.45} \tag{2}$$

and found[11] T = 3750 °K (W.B.S.) for pure graphite.

Waidner and Burgess do not give their value of R, but a simple calculation shows that $\lambda \ln R$ must be 0.0006978 to yield $T = 3750$ °K from Equation (2). To express this on the I.T.S. which is defined by

$$\frac{1}{t+273} = \frac{1}{1336} - \frac{\lambda \ln R}{1.432} \tag{3}$$

we substitute 0.00069785 for $\lambda \ln R$ in Equation (3) and find that $t + 273 = 3829$ °K (I.T.S.). The fact that R was not measured directly but in two steps, using a "convenient reference temperature" around 1625 °K does not alter the basis of their result. R is about 50,000 in this case, and such a brightness ratio is never measured in one step.

To compare the G.E.S. and the I.T.S. we must drag a "skeleton out of the closet." The experimental data[12] previous to 1929, all reduced to a common basis, yield a value for the palladium point of $T = 1553.1$ °C or $T = 1826.1$ °K (I.T.S.). More recently[13] a value of 1827.4 °K (I.T.S.) has been found at the National Physical Laboratory. The figure 1826.6 °K on the International Scale was found in our laboratory.[12] There seems but little doubt that the palladium point is within a few tenths of a degree of 1827 °K (I.T.S.). Now the basis of the G.E.S. is stated[6] as 1336 for the gold point, 1829 for the palladium point, and 1.433 for c_2. Two of these data are sufficient; three are too many. The three given are not consistent with Equation (1) and the experimental data on $\lambda \ln R$. The gold point should be raised 1.3°, the palladium point should be lowered 2.5°, or the value of c_2 changed to 1.428 in order to satisfy Equation (1). We understand that in actual practice,[7] the scale is based on the palladium point. That being the case 1829 °K (G.E.S.) = 1827 °K (I.T.S.) and 3800 °K (G.E.S.) = 3794 °K (I.T.S.).

Returning now to the measurements made on the arc as set up by the National Carbon Laboratory, Dr. N. K. Chaney operated his arc in our laboratory using four different positive electrodes, two lampblack and two graphite. The apparent temperatures which we obtained with our pyrometer from these arcs ranged from 3820 to 3822 °K (I.T.S.) A similar set of measurements by Forsythe and Watson at Nela Park yielded values for four arcs ranging from 3800 to 3815 °K (G.E.S.) whose average was 3805 °K (G.E.S.). Finally, measurements on six arcs at the National Carbon Laboratories yielded values ranging from 3808 to 3821 °K, average, 3814 °K (G.E.S.). These data are all given in Table D of the paper by Chaney, Hamister and Glass,[9] who derive therefrom a value of 3810 °K, with an uncertainty of 7°. They state "The melting point of Pd is taken as 1829 °K, based upon a value for the melting point of gold at 1336 °K—the constant C_2 of Wien's equation being taken as 1.433 cm deg," and further, in the footnote on page 118, that their pyrometer was calibrated by Dr. Forsythe. The values of 3805 °K and 3814 °K are therefore unquestionably on the same basis, which is not the basis for our value of 3821 °K. Reducing all results to a common scale, our result would be 13° higher than the National Carbon value and 22° higher than the Nela value. This would indicate a fairly satisfactory reproducibility of the source even though none of the differences be ascribed to experimental errors. However, the performance of the arc, as operated by Dr. Chaney in our laboratory, would indicate that these differences are not to be ascribed to variability of the arc.

Up to about 1922, the Nela Laboratory actually used melting palladium to maintain their scale which was then based[14] on 1828 °K for that point and $c_2 = 1.435$ cm deg. According to information[15] furnished us by Dr. Forsythe, the palladium point was thereafter realized for some fifteen years by sighting upon two 7.5-mil hairpin filament vacuum tungsten lamps, carrying the currents which comparisons during the ten years previous to 1922 had indicated would bring these lamps to the same apparent temperature, $T_{0.665\mu}$, as a blackbody at the palladium point. In 1937 Dr. Forsythe brought these lamps to our laboratory to see whether they had changed materially during the previous 15 years. We found that, at $\lambda = 0.665\mu$, the radient energy from these lamps was the same as that from a blackbody at 1829.9 °K (I.T.S.) in one case and 1829.4 °K (I.T.S.) in the other case, or 2.9° and 2.4° above 1827 °K (I.T.S.) which is the palladium point. These temperatures then correspond to 1831.9 °K (G.E.S.) and 1831.4 °K (G.E.S.) on the basis outlined. Thus, regardless of whether these lamps matched the palladium point in 1922 and subsequently changed, or whether they were assigned a temperature in 1922 which was 2° to 3° below their actual value on the G.E.S., the fact is that, in 1937, the scale *as realized at Nela Park* is much closer at the palladium point to the I.T.S. than to the *definition* of the G.E.S. Making a correction for this difference at the palladium point, the Nela value for the apparent temperature of the carbon arc becomes 3811 °K (I.T.S.), while the National Carbon value becomes 3820 °K (I.T.S.).

We feel that we are a little optimistic in believing that the scale we have set up in our own laboratory is in accord with the *definition* of the I.T.S. within ± 10° at 3800 °K. I would therefore put the apparent temperature of the carbon arc described by Dr. MacPherson at 3820 °K (I.T.S.) with an uncertainty of ± 15°. The arc is believed to be reproducible to better than that.

The true temperature is of less practical importance but of no less interest. Looking at Fig. 1 in Dr. MacPherson's paper, one can hardly escape the feeling that the peak of energy in the blue must surely make the color temperature, 3990 °K, higher than the true temperature. This is borne out by the value of 3860 °K obtained from the distribution. In view of the corrections necessary to get the true temperature by any other method, I would put most faith in the "distribution temperature" as representing the true temperature. However, Chaney, Hamister, and Glass report 3925 °K from a measurement of λ_{max}; I would therefore put the true temperature as between 3860 and 3925. This puts the spectral emissivity between 0.85 and 0.94—more in line with what we have reason to believe is the emissivity from other data. We have recently measured the emissivity of Acheson graphite from 1050 to 1400 °K and found it to be 0.924 and independent of temperature in that range. The surface of an arc electrode, because of its roughness, is probably blacker than the filament of a carbon lamp.

The data on the apparent temperature which have been discussed are summarized in Table 1 for convenience.

Table 1. Observations on the Apparent Temperature of the Positive Crater of the Carbon Arc.

Observers	Value Reported (°K)	Value on I. T. S. (°K)
Waidner and Burgess	3750	3829
Chaney, *et al.*	3814	3820
Forsythe and Watson	3805	3811
Wensel	3821	3821
Weighted Mean		3820 ± 15

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See for example: Kohn, H., and Guckel, M., *Z. Physik*, **27**, 5-6, 305 (1924); Voille, *J. de Phys. (3)*, **2**, 545 (1893); Lummer, O., "The Liquefaction of Carbon and Attainment of the Solar Temperature," Braunschweig, 1914.

See for example: Patzelt, F., *Z. techn. Physik*, **42**, 66 (1923); Waidner, C. W., and Burgess, G. K., *Bull. Bur. Standards*, **1**, 109 (1904); Blondel, *Proc. Int. Elec. Congress*, Chicago, 1893.

Bowditch, F. T., and Null, M. R., *J.O.S.A.*, **28**, 500 (1938).

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Forsythe and Worthing, *Abst.-Bull. G. E. Co. Nela Park*, **2**, 6 (1930). Quoting from page 6: "The temperature scale is that adopted by the General Electric Company's research laboratories. On this scale the melting-point of gold is 1336 °K, that of palladium 1829 °K, and the c_2 of Wien's equation is 1.433 cm deg." The palladium point was the reference point upon which the scale was actually based.

Private communication from W. E. Forsythe.

Today the best approximation to the thermodynamic scale would be obtained by assigning 1063 °C to the gold point, 1.436 cm deg to c_2, and using Planck's Law. The evidence indicates that this scale would not differ by more than 12° at 3800 °K from the thermodynamic scale. The difference between using Wien's Law and Planck's Law is less than 0.3° up to 3000 °K and less than 3° up to 4000 °K. See *J. Research N.B.S.*, **22**, 375 (1939).

Chaney, Hamister, and Glass, *Trans. Electrochem. Soc.*, **67**, 107 (1935).

Waidner and Burgess, *Bull. B.S.*, **1**, 109 (1904).

The figure of 3750° is deduced from their result of 3680 °K with one pyrometer, 3270 °K with another pyrometer, and their statement that "Pure graphite gives a temperature not over 50° higher." In another place they say that the apparent temperature of the pure graphite arc is at least as high as 3750 °K. This makes 3750 °K both the upper and lower limit of their result!

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14. Forsythe, W. E., *Abst.-Bull. Nela Res. Lab. G. E.*, **1**, 559 (1925).

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Temperature Measurement with Blocking-layer Photocells

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The authors' predominant interest in temperature-measurement problems of the steel plant naturally tends to limit the following discussion of temperature measurements with photocells; however, certain aspects of this discussion have more or less general applicability.

When work was started on this problem about ten years ago in the Research Laboratory of the United States Steel Corporation, the essential need in this field was for an accurate and preferably rapid method of measuring high temperatures which could also be used with recording instruments. The few thermocouples which could stand such temperatures (1300-1750 °C or 2400-3200 °F) were subject to rapid deterioration under the conditions of most practical applications. Optical pyrometers were applicable and reasonably accurate, but could not be used with recording instruments; the available total-radiation pyrometers were generally of poor design and subject to more or less serious errors, although they could be used with recorders.

The most promising lines of development seemed then to be (1) refinements in design of total-radiation pyrometers, and (2) the use of photoelectric cells. Since that time, in spite of some developments in thermocouples and protective tubes, and great progress in the design of total-radiation pyrometers, photocells have found increasing application in this field, and are either essentially equivalent or definitely superior for a number of applications.

Perhaps the earliest specific suggestion for the application of photocells for temperature measurement was made by Ives[1] in 1920. We shall not attempt to review here the rather scanty literature appearing on the subject since that time.

Nearly all our work has been done with the so-called "blocking-layer" or "rectifier" type of cell, such as the Photronic cell made by the Weston Electrical Instrument Corporation. Such cells usually have a "blocking" layer such as selenium, coated on a metal disc, with a thin, transparent layer of gold or platinum sputtered on top. The radiant energy passing through this transparent layer is absorbed near the upper surface of the blocking layer and sets free electrons which tend to flow to the transparent metal film. The cell thus consists merely of an arrangement for holding, protecting, and making stable electrical contacts to both sides of this thin metal disc. Compared to the common vacuum type cell with a glass bulb, it has the advantages of (1) ruggedness with respect to handling and rough usage, and a size and shape such as to facilitate the design of fixtures for holding and protecting it; and (2) the property of self-generation of its potential or current, which in many cases simplifies the electrical circuits involved and in other cases helps to avoid certain errors, such as those due to variable supply voltage.

Temperature-Voltage Calibration

If the cell is simply shunted with a rather low external resistance of the order of 50-300 ohms, either the current flow or the voltage drop across this resistance will approach very near to a straight-line variation with the intensity of illumination in foot candles. In picturing the response to a temperature change, the curves of Fig. 1 are helpful. Here the curve on the left shows the relative sensitivity-wave-length curve for the Photronic cell, and on the right are a few curves of wave-length vs. radiation intensity from a blackbody for various temperatures. Obviously, the temperature vs. output variation for the cell should depend on the relative change in the *common area covered* by *both* the sensitivity curve and the radiation intensity curve for any given blackbody temperature. By rough measurement, this common area turns out to vary with approximately the tenth power of the absolute temperature. This comparison immediately shows up two characteristics of photocells used as pyrometers.

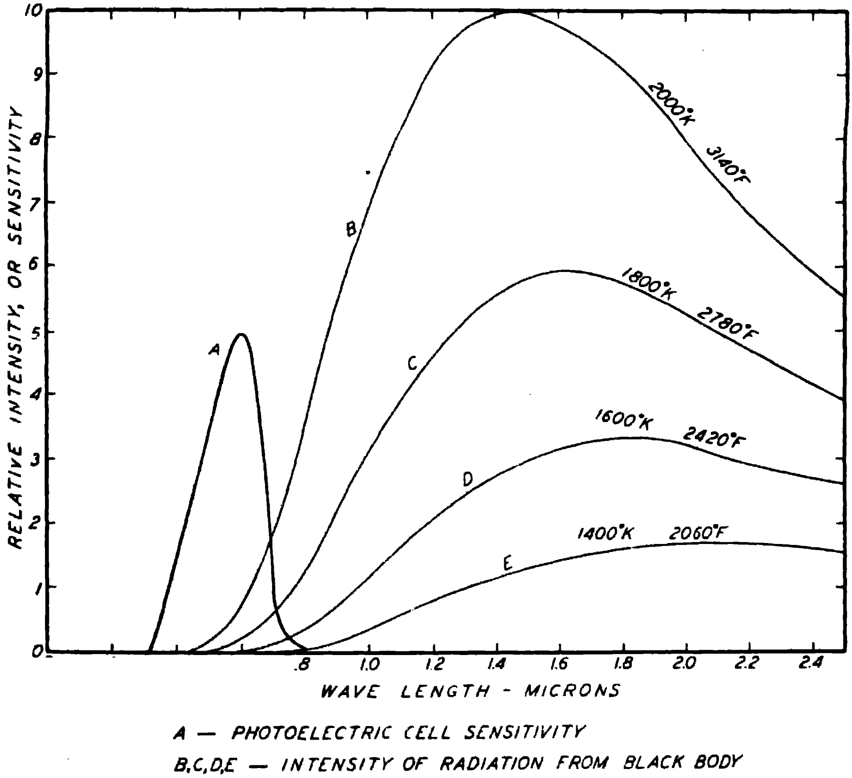

FIG. 1. Distribution of energy in the spectrum of a blackbody, compared with the sensitivity curve of the Photronic cell.

(1) The response curve will form a rapidly expanding temperature scale with an increasing accuracy toward higher temperatures, similar to that of an optical pyrometer. Incidentally, the sensitivity-wave-length curves of such photocells are rather close to that of the human eye.

(2) At furnace temperatures of 2000-3000 °F, the relatively small energy content in the short wave-lengths which affect the photocell are accompanied by a very much larger amount of useless infrared radiation, the relative proportion of the latter increasing with decreasing temperature. This is discussed again below in connection with the protection of cells from overheating.

Fig. 2 shows calibration data with a blackbody radiation source for two different photocells in different temperature ranges, and with the cells mounted in diaphragm tubes such as to give different included angles in the cone of incident radiation, the data being plotted as the logarithm of the cell output vs. the logarithm of the temperature (in °K). The data permit two parallel lines at a slope of 12.34 so that the potential drop (E) for presumably any cell of the same type with any arbitrary fixture design (assuming the whole cell face is illuminated) and over a fair range of shunting resistance (below a maximum of perhaps 200-300 ohms) could be expressed as

$$E = kT^{12.34} \qquad (1)$$

This agrees qualitatively with what we should expect from Fig. 1. In Fig. 3 the curves of Fig. 2 are replotted on ordinary linear scales.

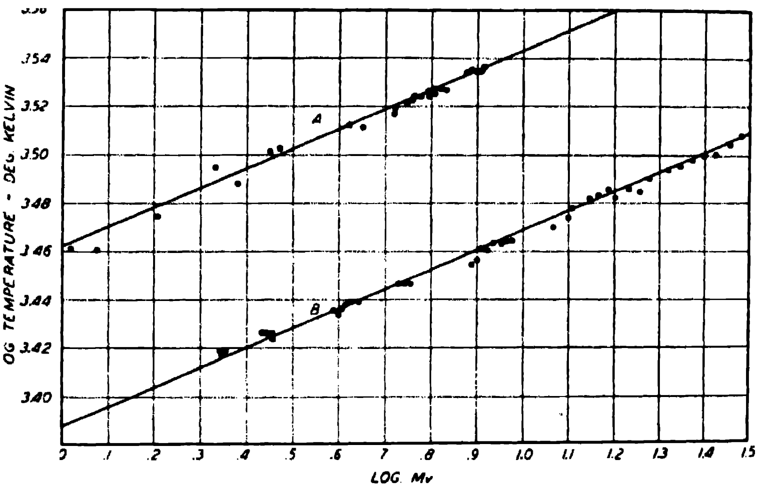

FIG. 2. Calibration curves for two Photronic cells, logarithmic scale.

This type of photocell in general is subject to uncontrolled variations in manufacture such as to cause differences in sensitivity not only between different cells but also between different areas on any one cell disc. However, it is claimed that for certain types, such as the Photronic cell used here, the relative wave-length-sensitivity variation is the same for various cells of a given type. This means that the constant k above would be the only variable as between different cells of one type, and if the calibration curve for the latter is known, the changes from cell to cell can be adjusted from a check at any single temperature. This is indicated by the parallelism of the lines in Fig. 2, and in general we have found it to be true, at least within the limits of accuracy of steel plant measurements.

In the mounting of such cells we have practically always found it preferable to avoid using lenses, and to set the cells at the end of a simple diaphragm tube in such manner that the whole face of the cell is illuminated. In such a unit the potential drop (E) across a shunting resistance (preferably not over 200-300 ohms) is given by

$$E = k\frac{SD^2}{L^2}T^C \qquad (2)$$

where C is the slope as in Fig. 2, T is absolute temperature, D is the diameter of the opening in the diaphragm, farthest from the cell face, which limits the cone of radiation, L is the distance between this diaphragm and the cell face, S is the sensitivity of the individual photocell, and k is a constant for all cells of the same type.

Thus it is possible to adjust for differences between cells or for changes in sensitivity of a given cell and for variations in fixture design simply by varying the value of the shunting resistance, and to check by either of two methods:

(1) The reading may be compared at any one temperature with that of an optical pyrometer on the source being measured or on some other known radiation source.

(2) The cell may be compared with a "standard" cell of the same type on any convenient constant source of radiation.

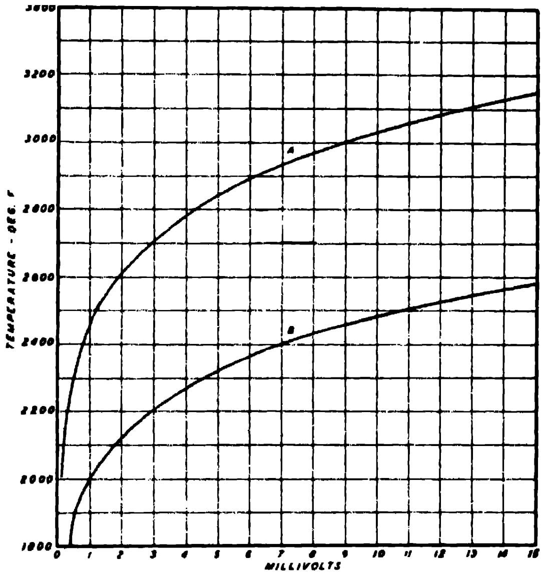

Fig. 3.

Calibration curves for the two Photronic cells of Fig. 2, ordinary scale.

Advantages and Limitations in Practice

Some of the advantages of such photocells for various practical temperature measurement problems are as follows:

(1) These cells are very rapid in response to changes in intensity of the incident radiation, rapid enough, for example, to indicate the passage of a rifle bullet across their field of vision. This makes possible certain applications where it is desirable either (a) to measure accurately temperature variations occurring in a period of a few seconds or less or (b) to have a very short total period of exposure at each measurement. In the recording of such cases it is the temperature recorder speed which limits the overall period involved.

(2) The rapidly expanding temperature scale makes possible a high degree of precision within a limited span near the top of any given temperature range, especially at the higher temperature levels. This is often useful in control of certain processes where a certain rather narrow optimum temperature range is involved in some fashion. A degree of precision equal to the best of optical pyrometer measurements is obtained, together with the possibility of recording the data on standard-type instruments.

(c) A cheap watchglass window in the front of the cell holder prevents occasional "shots" of steel or slag droplets from the furnace from reaching the filter glass or cell face behind it, and is easily replaced when so damaged. The glass filter behind it absorbs infrared radiation, most of which is dissipated in holder and tube before reaching the cell disc. The diaphragm tube is made sufficiently long and narrow to prevent nearly all shots of steel or slag from reaching the glass window.

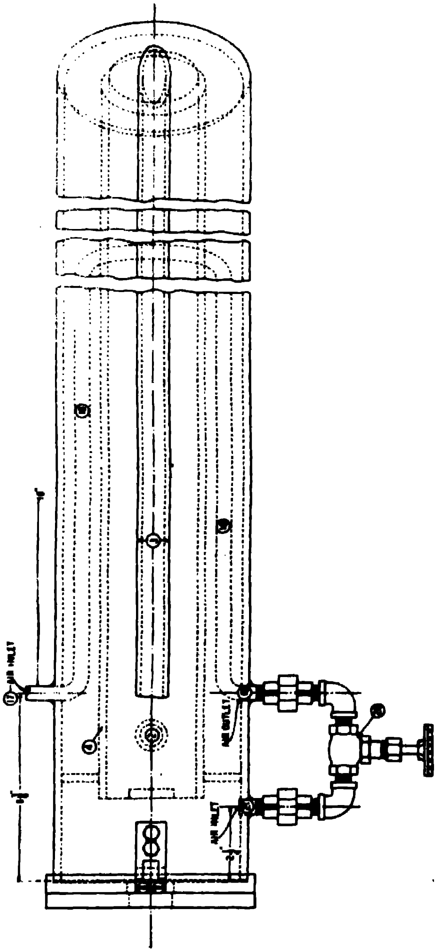

Fig. 4a.

Water-cooled fixture for Photronic cell as used in measuring open-hearth furnace-roof temperature.

(d) An air line is first passed through the water jacket and then into the space behind the cell-holder. This cooled air passes through channels in the cell-holder, through the diaphragm tube and out toward the furnace opening, serving the double purpose of dissipating the radiant-heat energy absorbed in these parts and of keeping the radiation path clear of all dust or fumes which might enter from the furnace chamber or other sources.

Some or all of the troubles indicated above will usually be absent in most applications. It should be noted that while direct or reflected sunlight or artificial illumination usually has a negligible effect on total-radiation pyrometer units, such

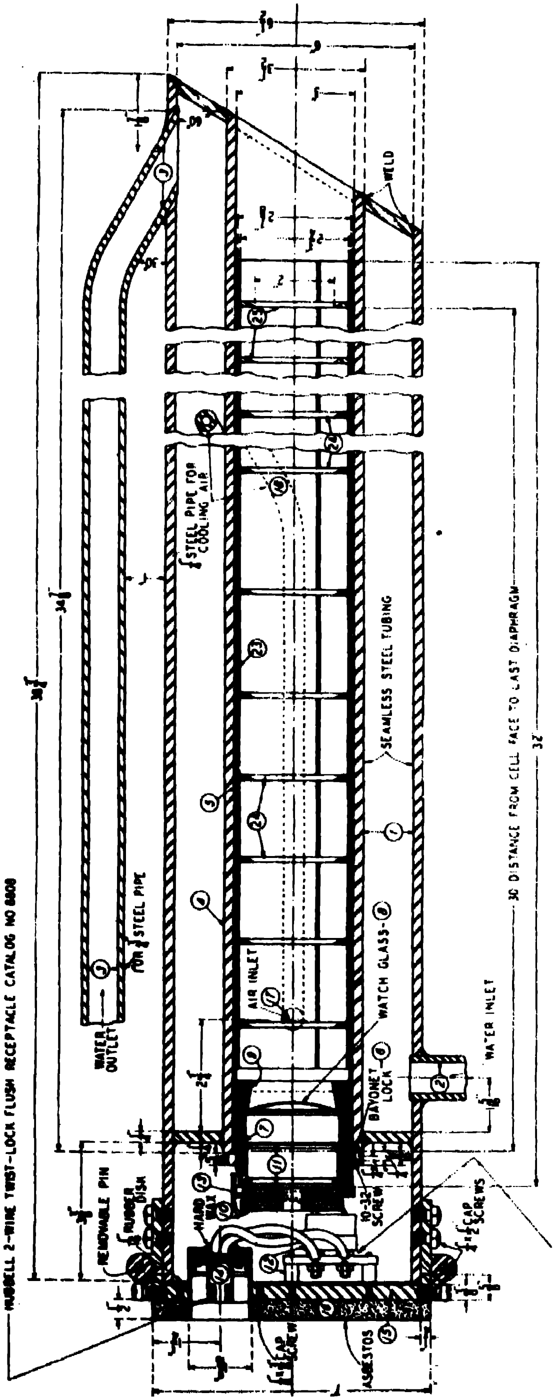
HUBBELL 2-WIRE TWIST-LOCK FLUSH RECEPTACLE CATALOG NO 8808
WATER OUTLET
STEEL PIPE
STEEL PIPE FOR COOLING AIR
WELD
SEAMLESS STEEL TUBING
30 DISTANCE FROM CELL FACE TO LAST DIAPHRAGM
32
AIR INLET
WATCH GLASS
BAYONET LOCK
WATER INLET
10-32 SCREW
CAP SCREWS
HARD WAX
RUBBER DISK
REMOVABLE PIN
CAP SCREW
ASBESTOS
PIN PLUG AND JACK—GENERAL RADIO TYPE 274

FIG. 4b. Detail of fixture in Fig. 4a.

radiation may cause very serious errors in photocell pyrometers and must be guarded against in certain applications.

It will perhaps be noted that we have referred mainly to "precision" rather than "accuracy" in the foregoing discussion. For the applications we have been interested in, it has been more important to obtain relative temperature values with reasonably high precision and with moderate accuracy; for such purposes these cells have been very satisfactory. There is probably room for more exact laboratory studies of the temperature-response characteristics of different cells made to one type by a given method of manufacture.

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A New Two-color Optical Pyrometer

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The monochromatic optical pyrometer fails if either the emissivity of the source or the transmission of the intervening space is unknown or variable.

The Wien Law

$$E_{\lambda_1} = c_1 \epsilon_{\lambda_1} \lambda_1^{-5} e^{-\frac{c_2}{\lambda_1 T}} \tag{1}$$

will provide only an "apparent" temperature if the emissivity, ϵ_{λ_1}, is unknown. If, however, it may be assumed that "grey" conditions exist so the ϵ_{λ_2} at some other wave-length is the same as ϵ_{λ_1}, then a second monochromatic optical pyrometer working at λ_2 may be used, according to the equation

$$E_{\lambda_2} = c_1 \epsilon_{\lambda_1} \lambda_2^{-5} e^{-\frac{c_2}{\lambda_2 T}} \tag{2}$$

Eliminating ϵ_{λ_1} $(=\epsilon_{\lambda_2})$ gives

$$\frac{E_{\lambda_1}}{E_{\lambda_2}} = \left(\frac{\lambda_2}{\lambda_1}\right)^5 e^{\frac{c_2}{T}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)} \tag{3}$$

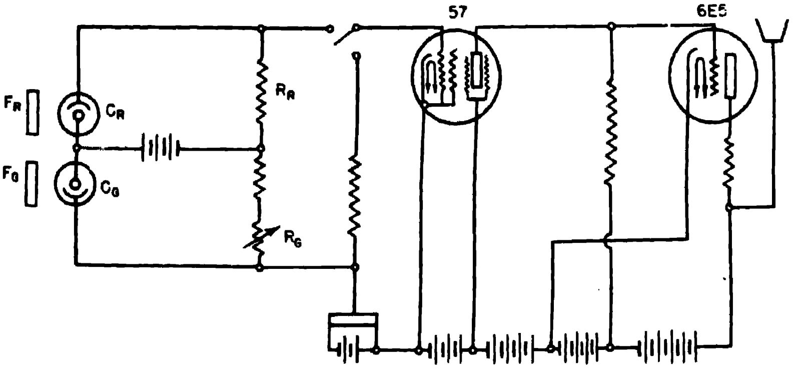

Fig. 1. Electrical circuit of the portable two-color photoelectric optical pyrometer.

Temperatures have been measured in the laboratory by the use of two pyrometers, one operating in the red and the other in the green; but obviously both the temperature and the emissivity must remain quite constant throughout the period of the measurements.

Equation (3) may be put in the form

$$\log \frac{E_{\lambda_1}}{E_{\lambda_2}} = A + \frac{B}{T}$$

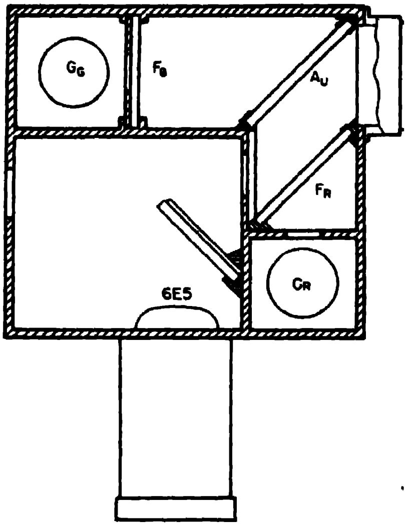

FIG. 2. Schematic drawing of the portable two-color photoelectric optical pyrometer head showing the optical system used in separating and filtering the incident radiation.

FIG. 3. The portable two-color photoelectric optical pyrometer being used to measure furnace temperature.

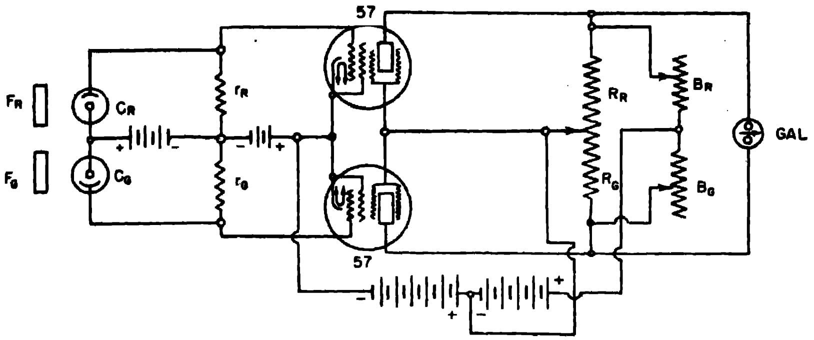

FIG. 4. Electrical circuit of the recording type two-color photoelectric optical pyrometer.

This indicates that, if the ratio of the intensities of two radiations of different wave-lengths is directly determined, it will provide a direct measure of the temperature. This further suggests the use of photoelectric cells and some electric circuit which will respond directly to the ratio of their outputs. The quantity A will then contain an instrumental constant which is dependent on the response of the circuit to E_{λ_1} and E_{λ_2}. The quantity B is fixed by the wave-lengths used.

A circuit which directly indicates a quantity proportional to the ratio of the intensity of two radiations is shown in Fig. 1. When the Wheatstone network consisting of the two cells, C_R and C_G, and the two resistances, R_R and R_G, is balanced by manually adjusting one of the resistances, the ratio of the photoelectric

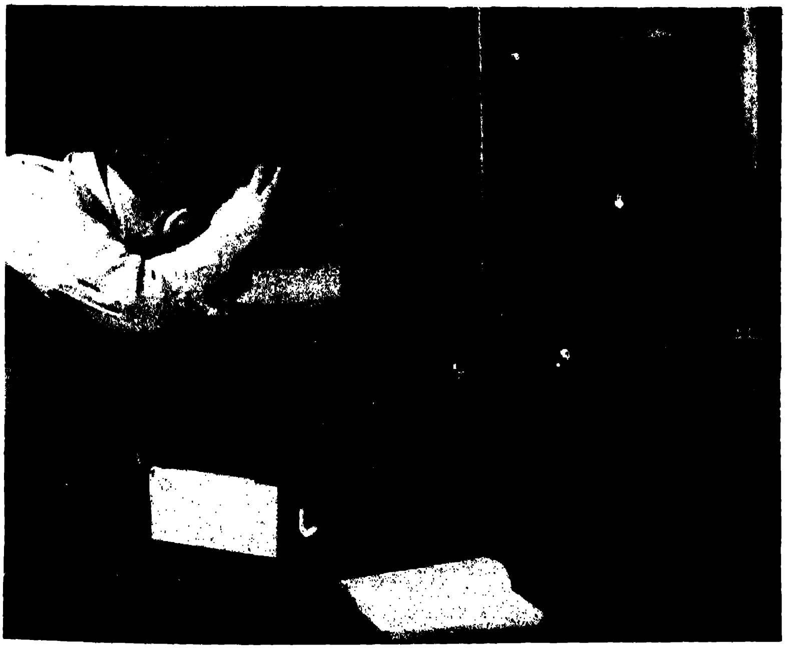

FIG. 5. A recording two-color photoelectric optical pyrometer being focused preliminary to recording furnace temperature.

currents is equal to the inverse ratio of the resistances. A 6E5 visual tuning tube is used as the null detector preceded by a 57-tube amplifier.

The pyrometer head is shown in Fig. 2. Light from the objective lens O strikes an inclined semi-transparent gold mirror, *Au*. The transmitted green light is passed on through a green glass filter, F_G, onto a photocell, C_G. The red reflected light passes through a red glass filter, F_R, onto the other cell, C_R. Vacuum type C_s-O-Ag cells are used to provide maximum stability with high resistivity. The pyrometer is sighted through the back peep-hole, on light reflected from the surfaces of the red filter. The null detector tube 6E5, contained in the handle, is visible at the same time in the mirror above it.

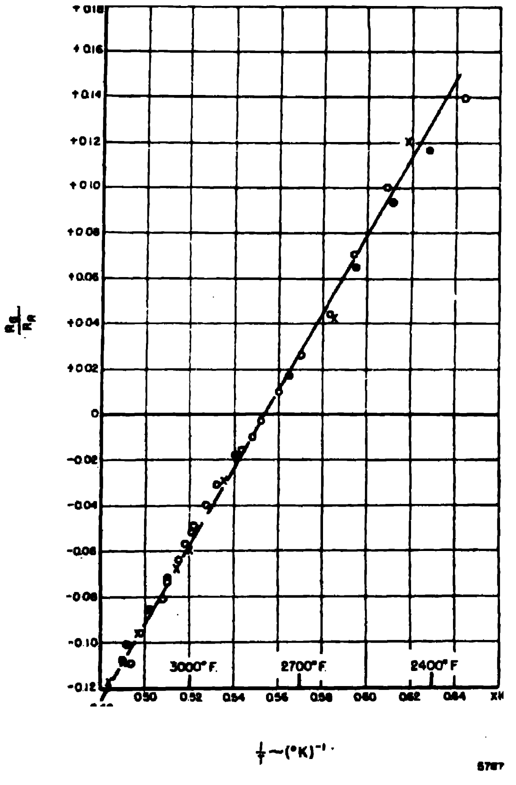

FIG. 6.

A plot of the data obtained on three separate days for calibration of the recording two-color photoelectric optical pyrometer. Inserted values in °F indicate relationship between °F and reciprocal °K.

Fig. 3 is a photograph of the entire instrument showing the pyrometer head, and the box containing the variable resistance and batteries. Part of the power is supplied as alternating current by a cord to a power pack in the box.

A less portable, but automatically recording form of two-color pyrometer has also been constructed. The electrical circuit is shown schematically in Fig. 4. In this instrument amplifying tubes 57 for each photocell, C_R and C_G, are contained in the pyrometer head, permitting the use of a low-resistance external circuit. The ratio determining resistance consisting of R_R and R_G is carried by the drum of a self-balancing recorder. Those portions of the plate currents which do not vary with the light intensity are balanced out by adjustable resistances, B_R and B_G in the circuit commonly used for this purpose. Switches, not represented, permit the galvanometer of the recorder to be used in this adjustment.

The recording type of pyrometer is shown in Fig. 5. The optical system of this pyrometer is essentially the same as that of the portable type. The cabinet at the right contains a power pack and voltage stabilizer and all the low-resistance circuit except the slidewire and galvanometer, which are in the recorder.

A calibration curve of the recording pyrometer is shown in Fig. 6. This contains data secured on three separate occasions on graphite crucibles heated in an induction furnace, comparison temperatures being secured by a disappearing-filament optical pyrometer. Note that the log of the ratio of the resistances varies linearly with the reciprocal of the absolute temperature. When the electrical characteristics of the circuit are changed, the curve is displaced parallel to itself; but, in agreement with theory, the slope remains unchanged if there is no change in the mean effective wave-lengths. Thus, under good conditions, a check at a single temperature could provide a calibration of the entire scale of the instrument.

The two-color pyrometers are operative on sources having temperatures over 1000 °C. Small high-temperature sources can be measured, but the results are subject to possible error because of variation of the sensitivity of the photoelectric cells from one point to another on their surface, so that in general the source should be large enough to fill the field stop. Reliable measurements at the temperature of molten plain-carbon steel can be secured even in the presence of a small amount of smoke. The fumes from high-manganese steel transmit the red selectively and seriously disturb the recordings.

The portable pyrometer is electrically the more stable but is not quite as sensitive as the recording pyrometer. Instability in the electrical circuit of the recording pyrometer has not yet been entirely eliminated, so that adjustments must be made about every half hour. An unexpected difficulty arises from the fact that an ordinary red glass filter varies in transmission as its temperature varies. This has not yet been corrected. At present the readings of the pyrometer are subject to errors of about 10 °C.

Temperature Radiation Emissivities and Emittances

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Introduction

The word emissivity comes from the Latin *emittere*, meaning to send out. In accord with that primary meaning, an emissivity for a given material is a measure of the ability of a body made of that material to send out radiant energy. Such an ability might be expressed in terms of the rate of emission per unit of surface area. Some use the word *emissivity* in this sense, and speak of an emissivity of 50 watts/cm^2, for instance; but general usage now expresses this ability differently. A comparison is made instead with a like ability of a complete or perfect emitter, a blackbody, at the same temperature.

In the interior of an opaque body of uniform temperature throughout, at distances from its surfaces yielding practically complete absorption for entering radiation, blackbody conditions are found. If the body is a blackbody, the rate of emission of radiant energy from its surface will correspond to the unhindered passage of radiant energy from such an interior. If the body is a non-blackbody, the rate of emission will be lessened because of the hindrance, in the way of reflection, occurring at the surface. With these facts in mind, it is natural to express a sending out ability, that is an emissivity, for non-black material as a ratio, that for an opaque body composed of the non-black material to the corresponding ability for a blackbody at the same temperature.

In accord with the usage that an *ivity* ending shall denote a characteristic of a material, the term *emissivity* is limited to a comparison with a blackbody under conditions where the individual characteristics of bodies composed of the material under consideration are eliminated. Since the radiating characteristics of a body depend in part upon its opaqueness and the roughness of its surface, these features must be considered in forming an acceptable definition of emissivity. Ease of specification and of reproduction are the obvious reasons for requiring that the emissivities of materials shall refer to comparisons made with opaque specimens whose surfaces are polished. Accordingly, the emissivity of a material is defined as the ratio of a rate of emission of radiant energy by an opaque body with polished surface composed of that material as a consequence of its temperature only, to the corresponding rate for a blackbody at the same temperature. Thus, the rate of emission of radiant energy per unit area by tungsten at 2000 °K is 23.7 watts/cm^2, the corresponding rate for a blackbody is 91.8 watts/cm^2, and the hemispherical total emissivity of tungsten at 2000 °K is 0.258. There are several types of emissivity.

Two other terms, namely emissive power and emission factor, have been and are still used to some extent to indicate what we now mean by emissivity. It is also true that, to some extent, as stated above, the term *emissivity* has been and is used to designate the quantity now called radiancy.

In accord with the usage that an *ance* ending shall denote a characteristic of a body or of a portion of a body rather than of the material composing it, an emittance for a body at some constant temperature is defined as the ratio of a rate of emission of radiant energy by the body in consequence of its temperature only to the corresponding rate for a blackbody at the same temperature. The condition of the surface of the body, polished or not, oxidized or not, and the condition as to opaqueness are immaterial. For a tungsten filament at 2000 °K, whose surface has been roughened greatly, a hemispherical total emittance of 0.5 in contrast with the corresponding emissivity of 0.258 is not impossible. If the body is opaque, the emittance has the emissivity as its lowest limiting value. For a glass rod at 1000 °K, however, due to its nonopaqueness, one expects emittances less than the emissivities. In place of a normal spectral emissivity of about 0.96 for visible light, one may obtain a corresponding emittance of say 0.10. Often the emittances of composite bodies, as of a shellacked piece of steel, are of interest. Their probable values range from zero to unity.

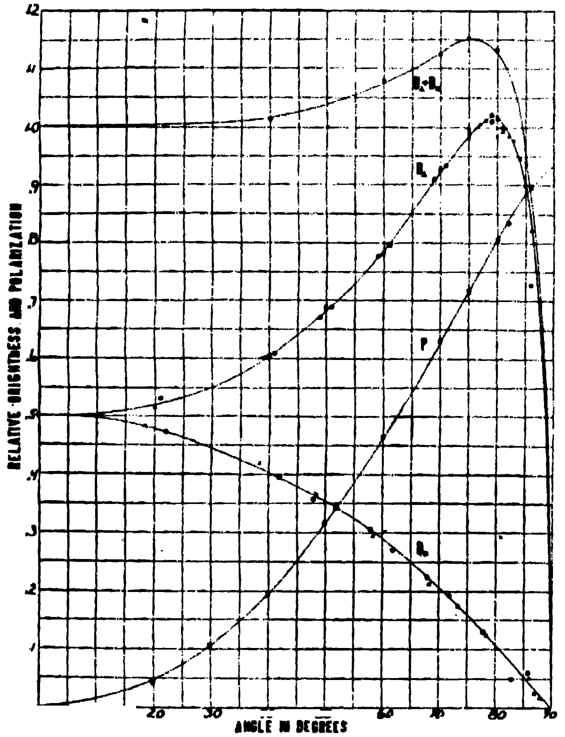

Fig. 1.* Showing for tungsten, at temperatures ranging from 1750 °K to 2470 °K, relative spectral brightnesses ($\lambda = 0.665\mu$) for the principal polarized light components $B_\perp$ and $B_\parallel$ and the natural light $B_\perp + B_\parallel$ and the polarization of the natural light P. The variation from Lambert's cosine law is shown by the $B_\perp + B_\parallel$ curve, as well as the variation of the emissivity $\epsilon_{\theta\lambda}$ with angle of emission. The $B_\perp$ and $B_\parallel$ curves show similar emissivity variations for the two corresponding polarized components.

Types and Definitions

There are various standpoints from which a non-blackbody's radiating ability may be considered. The two most common are the total heating effects per unit area, taking account of all wave-lengths of radiation, and the spectral heating effects, taking account of only a very limited range of wave-lengths. Corresponding thereto we have total and spectral emissivities. If the standpoint is one of visual effects rather than of heating effects produced by the radiation, we obtain a luminous, or visible, emissivity. Corresponding to a comparison with a blackbody, not at the same temperature but at the same visual color instead, we speak also of a color emissivity. Other emissivities, such as an erythermal emissivity, might be defined, but the writer is not aware of their actual use.

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* Illustrations for this paper supplied through the courtesy of *Journal of Applied Physics.*

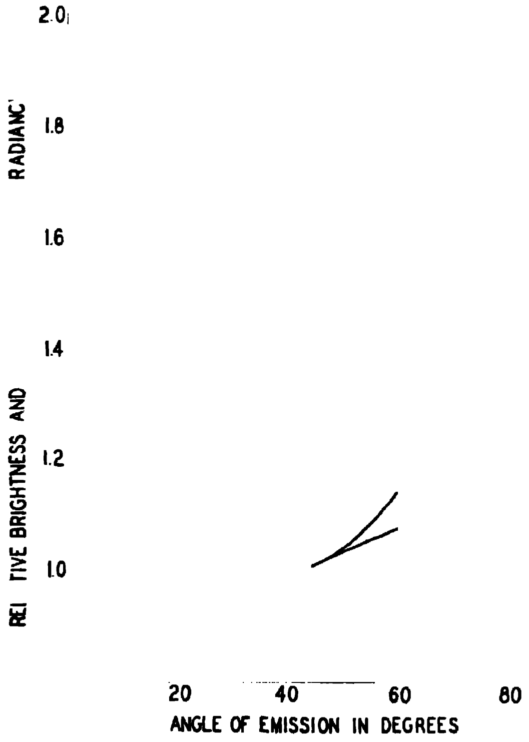

Fig. 2.

Showing for platinum, at incandescence, the variation (a) of total steradiancy, and (b) of spectral brightness in the red with angle of emission.

For each of the foregoing types of emissivity, at least two subdivisions are to be recognized, a normal and a hemispherical emissivity. The cause for this is the departure from Lambert's cosine law exhibited by the radiation from non-blackbodies. Illustrations of such variations are shown in Fig. 1 spectrally for tungsten[44] and in Fig. 2 totally for platinum.[2] One might, if one wished, speak also of an emissivity at any prescribed angle with respect to the normal. Such emissivities are not commonly listed, however.

In giving precise definitions for the various emissivities, we need, in describing radiation sources, to make use of three well-recognized terms and a fourth which is not well-recognized. They are[8] radiancy, steradiancy, brightness, and "luminous radiancy." The radiancy of a source of radiation is its rate of emission of radiant energy per unit of area. It is commonly expressed in watts/cm^2. The steradiancy of an element of a source of radiation in a given direction is its rate of emission of radiant energy in that direction per unit area and unit solid angle. It is commonly measured in watts/(cm^2 steradian). The brightness of an element of a source of radiation in a given direction is its rate of emission of light in that direction per unit area and unit solid angle. It is analogous to steradiancy and is commonly expressed in lumens/(cm^2 steradian) or in candles/cm^2. The "luminous radiancy" (the not well-recognized term) of a source of light is its rate of emission of light per unit of area. It is analogous to radiancy and is expressed in lumens/cm^2.

We are now ready to give precise definitions for the various emissivities, each of which is defined for an element of polished surface of an opaque body at constant temperature.

A hemispherical total emissivity, ϵ_{ht}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its radiancy to that of blackbody material at the same temperature.

A normal total emissivity, ϵ_{nt}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its normal steradiancy to that of blackbody material at the same temperature.

A hemispherical spectral emissivity, $\epsilon_{h\lambda}$, for the polished surface of an opaque portion of material at constant temperature is the ratio of its spectral radiancy to that of blackbody material at the same temperature.

A normal spectral emissivity, $\epsilon_{n\lambda}$, for the polished surface of an opaque portion of material at constant temperature is the ratio of its normal spectral steradiancy to that of blackbody material at the same temperature.

A hemispherical luminous emissivity, ϵ_{hl}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its "luminous radiancy" to that of blackbody material at the same temperature.

A normal luminous emissivity, ϵ_{nl}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its normal brightness to that of a blackbody material at the same temperature.

A hemispherical color emissivity, ϵ_{hc}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its "luminous radiancy" to that of blackbody material having the same color as viewed visually.

A normal color emissivity, ϵ_{nc}, for the polished surface of an opaque portion of material at constant temperature is the ratio of its normal brightness to that of blackbody material having the same color as viewed visually.

In usage there has been considerable confusion due to a failure to distinguish between hemispherical and normal emissivities. This has been particularly true of total emissivities.

Emissivities, both spectral (Fig. 1) and total (Fig. 2), vary with the emission angle. The definitions for the various types belonging to this group are obvious. They may be designated by $\epsilon_{\theta\lambda}$, $\epsilon_{\theta t}$, $\epsilon_{\theta l}$, and $\epsilon_{\theta c}$. Types of emittances are equal in number to the types of emissivities, and we properly speak of the hemispherical total emittance of a body and of its normal spectral emittance. Emittances will be distinguished by primes, thus ϵ_{nt}', ϵ_{ht}', $\epsilon_{h\lambda}'$, etc.

Closely connected with the terms *emissivity* and *emittance*, in theory and practice, are the terms *reflectivity* and *reflectance*, and *absorptivity* and *absorptance*. A *reflectivity* is defined for an opaque, polished portion of material as the ratio of a rate of reflection of radiant energy from its surface to the corresponding rate of incidence of radiant energy upon it. An *absorptivity* is defined for an opaque, polished portion of material as the ratio of a rate of absorption of radiant energy by it to the corresponding rate of incidence of radiant energy upon it. Since all the radiant energy which is incident on an opaque element of surface is necessarily either absorbed or reflected, the sum of a reflectivity and its corresponding absorptivity is necessarily unity. As with emissivity, we speak of spectral and total, normal and hemispherical reflectivities and absorptivities.

For an opaque-walled cavity which has a uniform temperature throughout and is therefore in equilibrium, it is easy to show that a body in the interior is emitting radiation from its surface at just the rate that it is absorbing radiation from the walls, which is incident on its surface. Not only is this true for total hemispherical rates of emission and absorption, but it is also true for the normal and the spectral rates for the conditions described, generally known as blackbody conditions. We may therefore write

$$(\epsilon = a = 1 - r)_T, \tag{1}$$

the subscript T at the right indicating that not only the ϵ, the a, and the r are for the temperature T, but that the incident radiations also are such as occur in a blackbody cavity at the temperature T. The equation then holds separately for each type of ϵ, a and r.

If, however, the incident radiation has a spectral distribution different from that characteristic of a blackbody at the temperature of the element of surface in question, the simple relations given in the equation no longer hold for the total emissivities. The corresponding spectral values for ϵ, a and r are, however, as one will perceive, independent of spectral distributions, and are therefore completely interrelated at all times by Equation (1) as shown. To illustrate, for tungsten at 2000 °K, $\epsilon_{n\lambda}$ at 0.665μ is 0.435 and the corresponding absorptivity and reflectivity values are 0.435 and 0.565. The value of ϵ_{ht} for the same temperature is 0.260, but what the values of a_{ht} and r_{ht} are cannot be stated unless the spectral distribution of the incident radiation is known. If it is that of blackbody radiation corresponding to 2000 °K, a_{ht} and r_{ht} are 0.260 and 0.740.

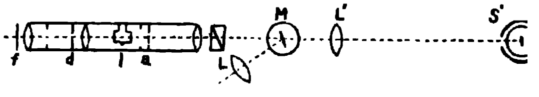

Fig. 3. Arrangement of apparatus for obtaining spectral emissivities by a reflectivity method in the visible region. S is a nearly enclosed light source, M a lamp containing a ribbon filament whose reflectivity is to be measured, Q a Rochon double image prism, L a lens imaging S on the ribbon filament, P a disappearing filament pyrometer with pyrometer lamp at l, absorbing screen at a, limiting diaphragm at d, and colored pyrometer glass filter at f. S, L, and M are supported on a rotatable mount with a vertical axis at the center of M. S' and L' are positions corresponding to S and L for the determination of the unreflected brightness of the image of S.

Measurement of Spectral Emissivities

Optical Constants Method. In texts on physical optics are shown (1) the dependency of the reflectivity and the emissivity of a material on its optical constants, that is upon its index of refraction and its absorption coefficient, and (2) how these constants may be determined experimentally. For further details regarding the optical constants method, such texts should be consulted.

Reflectivity Method for Obtaining $\epsilon_{n\lambda}$. This method for obtaining a spectral emissivity depends upon the relation

$$\epsilon_{n\lambda} = 1 - r_{n\lambda}, \tag{2}$$

or upon the corresponding relation in case $\epsilon_{h\lambda}$ is desired. In either case, the experimental procedure involves three determinations of spectral brightness or of spectral steradiancy.

To illustrate, suppose that one wishes to determine $\epsilon_{n\lambda}$ for tungsten, say at 1500 °K, in the visible region. As the tungsten specimen, let him select a uniform, polished ribbon mounted in a glass lamp bulb which is either evacuated or contains an atmosphere which does not react chemically with the tungsten, and, as an arrangement of apparatus, that of Fig. 3, except that the double-image Rochon prism, Q, may be eliminated if one is not interested in polarized components. Let $B_{\lambda 1}$ be the spectral brightness of the mirror resulting from its own high temperature, $B_{\lambda 2}$ that of the source, S, in position S' as seen, with M slightly displaced, through the bulb containing the polished tungsten ribbon, and $B_{\lambda 3}$ that of the source in position S as seen reduced by reflection from the mirror ribbon, superposed on the spectral brightness which results from the mirror's own high temperature. The reflectivity $r_{n\lambda}$, as a first approximation, is then given by

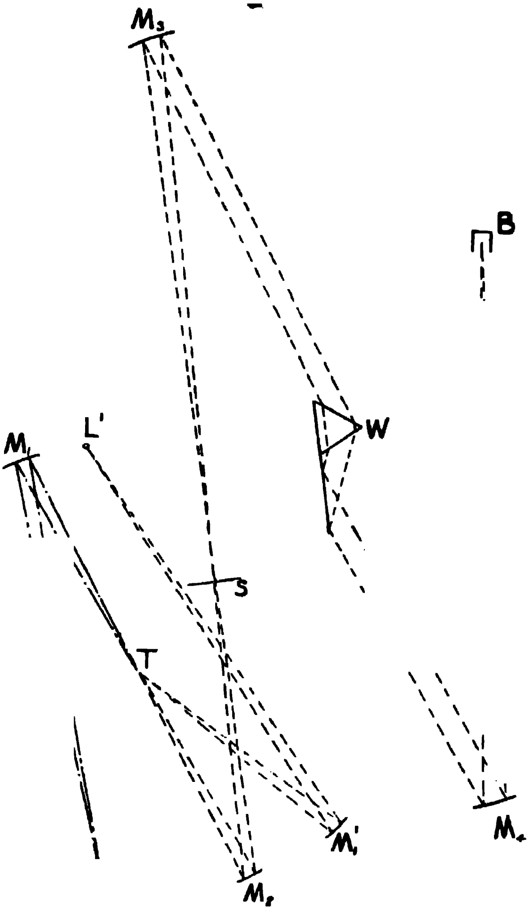

FIG. 3a.

Diagram showing apparatus used by Weniger and Pfund,[42] in the determination of normal spectral emissivities $\epsilon_{n\lambda}$ in the infrared.

$$r_{n\lambda} = (B_{\lambda 3} - B_{\lambda 1})/B_{\lambda 2}. \qquad (3)$$

Strictly speaking, one obtains thus an $r_{\theta\lambda}$ where θ is half of the angle between the line *SM* of Fig. 3 and the axis of the pyrometer. The correction to be applied to yield $r_{n\lambda}$, when not negligible, may be obtained by extrapolation. Equation (2) serves for obtaining $\epsilon_{n\lambda}$. Inspection shows that no corrections need be made for absorption of light by the glass of the bulb enclosing the mirror, *M*. For accuracy it is desirable that $B_{\lambda 1}$ shall be considerably less than $B_{\lambda 2}$.

The method described has been much used by the writer[44] not only for determining $\epsilon_{n\lambda}$, but also $\epsilon_{\theta\lambda}$ for various angles of emission and for the two normal polarized components of emitted light as well as the light taken as a whole.

Langmuir[19] applied this method to tungsten at its melting point. In a molten terminal of a metal arc there may be seen mirrored images of several orders, the first being that of the opposing terminal, the second that of the first terminal mirrored in the second, etc. Spectral brightnesses just inside and just outside such a first-order image for terminals just alike and at the same temperature, yield as above the $r_{\lambda n}$ and then $e_{\lambda n}$.

Shackelford,[33] using a somewhat open helical coil of polished tungsten ribbon which was heated electrically to a uniform temperature, likewise measured the spectral brightness of the ribbon within the coil just inside and just outside an image. Values for $\epsilon_{n\lambda}$, as in the case of Langmuir's measurements, followed simply.

Obviously the procedure outlined may be used in the infrared region, as was done by Weniger and Pfund[42] (Fig. 3a). Of course a receiver responding to the thermal effects of radiation was substituted for the pyrometer.

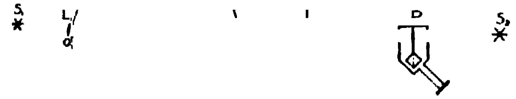

FIG. 4. Apparatus for the determination of a hemispherical emissivity in the visible region. *U*, Ulbricht sphere, *T*, polished hemispherical target, *M*, plane mirror, S_1S_2 light sources, L_1L_2 lenses, *N*, opaque screen with opening to just include the image of *T* formed by L_2. *P*, photometer head, *F*, filter for yielding approximately monochromatic light of the desired wave-length.

Reflectivity Method for Obtaining $\epsilon_{h\lambda}$. To obtain a hemispherical spectral emissivity by a reflection method is equally simple in theory, though not so in practice. A most direct method for the visual region employs the Ulbricht sphere of spherical photometry with its inner coating of highly reflecting and highly diffusing paint. A small, polished hemisphere, *T*, (Fig. 4) of the material being studied with the convex surface symmetrically oriented with respect to the photometric axis replaces the ordinary target. The source, *S*, supplying the light within the sphere should be so located that initially as much as possible of its utilized luminous flux shall be incident on a small portion only of the inner surface of the sphere back of the target, *T*, on the axis of the system at *O*. Insofar as the paint is perfectly diffusing, the remainder of the inner surface, except for the two small openings, will then be uniformly bright and will illumine the hemisphere uniformly. Under these conditions, the ratio of an average spectral brightness of the small hemisphere as viewed by the reflected light, less its own natural spectral brightness, to the corresponding spectral brightness of the inner surface of the large sphere, yields a corresponding $r_{h\lambda}$, and finally by means of Equation (2) the $\epsilon_{h\lambda}$ sought.

An appropriate filter, F, of Christianson or other type, yields the wave-length desired. An averaged spectral brightness for the hemisphere, ${}_1B_{h\lambda}$, is assured by having its image just fill the opening in the screen, N. Comparisons are made in the standard manner with the auxiliary source, S_2. An ordinary optical pyrometer cannot be used because the hemispherical surface ordinarily will not be uniformly bright. However, a photoelectric cell with a sufficiently large aperture placed back of N may be safely used. A determination of the brightness of the inner surface of the large sphere involves replacing the hemispherical mirror with a plane mirror of known $r_{n\lambda}$ with axis slightly tilted with respect to the photometric axis. The screen opening at N is then completely filled with light reflected from the inner surface of the sphere. A comparison of this image at N of spectral brightness ${}_2B_{h\lambda}$ with the auxiliary source, S_2, is made as before. It follows that

$$\epsilon_{h\lambda} = 1 - r_{h\lambda} = 1 - {}_1B_{h\lambda}/{}_2B_{h\lambda}. \tag{4}$$

The foregoing method has not actually been used so far as the writer knows. Perhaps there has not been sufficient need for the emissivity thus measured. An approximation to this method however, has been used by Prescott and Morrison[32] in a determination of the surface temperature of an oxide-coated filament. Because of the variability of oxide coatings for filaments in practice and because of the low thermal conductivity of the oxide layer, measurements with an optical pyrometer of the temperature of a coated tubular filament with its wall pierced by a small hole are not satisfactory. In place of the sphere, Prescott used a cylindrical tube lined with white, fluffy cotton which was lighted up by two automobile headlight lamps at opposite ends of the tube. A lamp with the oxide-coated filament was mounted with filament along the axis of the tube. An optical pyrometer was used to measure the spectral brightnesses (1) of the oxide surface with the headlight lamps unlighted, (2) of the oxide surface with the headlight lamps lighted, and (3) of the cotton lining with the headlight lamps lighted. The further procedure for obtaining an $r_{h\lambda}$ and an $\epsilon_{h\lambda}$ is evident. Strictly, the emissivity obtained was neither normal nor hemispherical, since the average brightness was for a cylindrical surface.

To obtain in a similar way a hemispherical spectral emissivity wherever desired in the infrared, using receivers responding to the thermal effects of radiation, would seem quite practicable. Inner surface coverings for the sphere which are generally highly reflecting and highly diffusing throughout the infrared, such as a diffusing aluminum paint, and selectively reflecting materials for filter purposes are both available.

Direct Brightness and Steradiancy Comparisons. In accord with the definition of an emissivity, these methods employ direct comparisons of a spectral brightness or a spectral steradiancy of the body (a non-blackbody) with that of a blackbody at the same temperature. Often, but not always, the material of the non-blackbody also forms that of the blackbody, and in such instances the condition of a common temperature for the two bodies is easily attained.

Le Chatelier, according to Burgess,[5] was the first to use the blackbody characteristic of a cavity in determining the brightness temperature, S_λ, true temperature, T, relations for a non-blackbody. Since S_λ and T are connected with ϵ_λ by the relation

$$\ln \epsilon_\lambda = \frac{c_2}{\lambda}\left(\frac{1}{T} - \frac{1}{S_\lambda}\right). \tag{5}$$

a relation such as $S_\lambda = f(T)$ leads at once to ϵ_λ as a function of T.

It was Mendenhall,[26] however, who in 1911 first proposed the open-V wedge device as a practical method for assuring equality of temperature for the black- and the non-blackbodies which were to be compared. The procedure was simple and a considerable impetus to the study of high-temperature radiations was given thereby. For polished material, as is evident from Fig. 5, the brightness viewed along *OA* is a composite brightness, being the sum of the natural brightness of *A* for the direction *AO*, the natural brightness of *B* once reflected, that of *C* twice reflected, that of *D* three times reflected, that from *C* directed toward *D* four times reflected, etc., in all seven terms. In equation form this yields for the spectral brightness of the wedge opening ${}_wB_\lambda$

$$ {}_wB_\lambda = {}_nB_\lambda(1 + r_\lambda + r_\lambda^2 + \dots r_\lambda^6), \tag{6} $$

where ${}_nB_\lambda$ is the natural spectral brightness of the wedge material. Though, strictly speaking, ${}_nB_\lambda$ varies with the angle of emission, that variation is immaterial here. Were the series of Equation (6) infinite, the right-hand member would represent the spectral brightness of a blackbody at the temperature of the wedge, ${}_bB_\lambda$. In the case of a 10°-wedge, the departures of the wedge opening from blackness $({}_bB_\lambda - {}_wB_\lambda)/{}_bB_\lambda$ amount, respectively, to 0.0001, 0.0016, 0.018, 0.16 and 0.40 for spectral reflectivities of 0.60, 0.70, 0.80, 0.90 and 0.95. Such a wedge is seen to be suitable for a blackbody, if the spectral reflectivity is of the order of 0.75 or less; and, where such is the case, the spectral emissivity $\epsilon_{n\lambda}$ may be taken as the ratio ${}_nB_\lambda/{}_wB_\lambda$, the ${}_nB_\lambda$ being measured in the direction *PQ* (Fig. 5). This method was considerably used by Mendenhall and Forsythe,[27] Spence,[34] McCauley[25] and others.

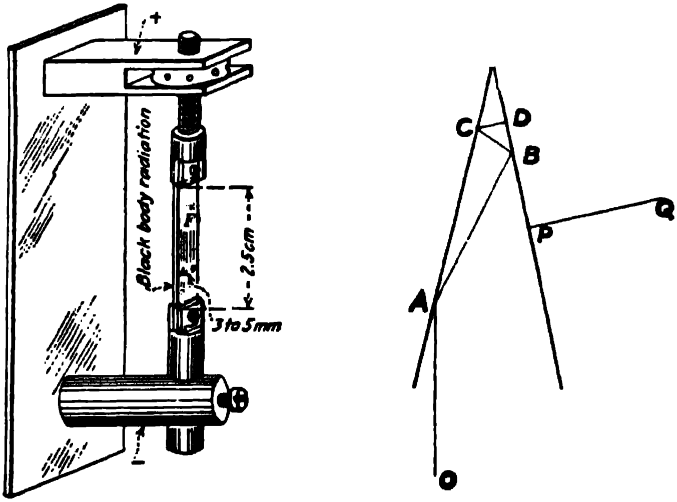

FIG. 5. Mendenhall's open-V, blackbody wedge.

The open-V wedge fails if the surface is not polished, but polishing ordinarily does not represent a serious difficulty. There are certain real difficulties, however. If the wedge is formed from a single sheet of material, a bulge will form on the inside at the sharp edge. If formed from two sheets instead, a slot is quite likely to be produced when the wedge is heated. Both effects are very serious so far as blackbody conditions are concerned.

The best method for obtaining blackbody radiation whose temperature is the same, or very nearly the same, as that of the material under study, where the heating is done electrically, seems to be that of shaping the material into a uniform tube with small holes through its sidewall. This was first done * in a satisfactory manner in the writer's [45] study of the emissivity of tungsten (Fig. 6). In this case, the tungsten tube was formed by extruding, through an annular die, tungsten powder which had been mixed with a binder. The holes were punctured shortly after the extrusion. The blackening of the radiation for a somewhat slantwise angle of emission from such a hole is nearly complete, and independent of the polish which may or may not be present on the inner surface of the tube. If the thermal conductivity of the material is known, correction may be made for the difference in temperature between the internal and external surfaces of the tube wall. An emissivity obtained by comparing an external surface brightness with that of an adjacent hole would seem to be free from error of method. In some instances, as for Pt, Pd, Au, and steel, small tubes may be purchased from supply houses. With small holes properly drilled, these tubes are quite as satisfactory as those just described.

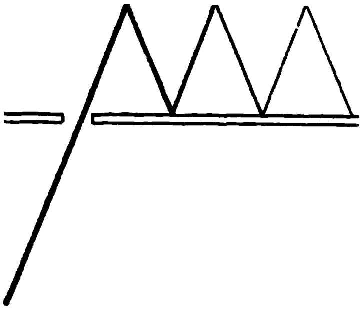

FIG. 6. Diagram showing how radiation through a small hole in the side wall of a uniformly heated tube builds up to form blackbody radiation.

The methods described for obtaining tubes with small holes in the sidewalls are not always convenient or possible. In that case, one may use a ribbon with small holes drilled through it, as has been done by Wahlin [39] and his co-workers,[48] and roll it around a mandrel to form a complete tube with opposite edges of the ribbon touching along a line parallel to the axis of the tube. Such tubes would seem to be nearly if not quite as satisfactory as the tubes which have been described. Still another method of obtaining a tube consists in winding a narrow ribbon, such as may be obtained by rolling down a circular wire, on a mandrel to yield a tightly closed spiral. Previous to the winding, the edges of the wire should be notched slightly to yield the desired holes leading to the interior. This method was used by the writer [46] in a study of the emissivities of molybdenum. Such blackbody tubes are definitely inferior to those previously described.

When the spectral emissivity of one metallic substance is known, that of a second metallic substance may be obtained by direct comparison. In making such

* Pirani in 1911 made use of a somewhat similar method. He used a carbon tube in whose wall, side by side, were a small hole leading to the center and a small imbedded sample of the material being studied. Because of (1) the relatively large unknown temperature differences between tube center and tube surface, (2) the diffusion of carbon into metals which takes place at high temperatures, and (3) the temperature variations likely to occur on account of the variations in material, Pirani's method has not proved satisfactory.
]

a determination for tantalum by comparison with molybdenum, the writer fused end to end two equal-sized filaments, one of molybdenum and one of tantalum, mounted them as a lamp filament, heated them to incandescence, observed their spectral brightnesses as functions of the distances from their junction, extrapolated such brightnesses for short distances to the junction, and computed the emissivities for the tantalum on the basis that the extrapolated spectral brightnesses corresponded to a common temperature. This is not recommended as a primary method because of the alloying action of the metals while being fused, as well as afterwards when the junction is at a high temperature. The results obtained for molybdenum by this method chceked well with those obtained otherwise.

Thus far tubular blackbodies have been used chiefly for visual studies, probably because of the larger holes in the sidewalls, the larger tube and consequently the larger heating currents that would be demanded for receivers other than the eye.

Spectral emissivities for a material are also obtainable from comparisons of spectral radiancy curves of the substance at a given temperature. Assuring, where incandescent temperatures are concerned, that the two temperatures involved are precisely the same is the main drawback to this method. Could one rely upon the Mendenhall open-V wedge to yield blackbody radiation, as was hoped for by McCauley [25] in his studies, such methods would be highly satisfactory. For temperatures which can be measured and regulated precisely with the aid of thermocouples, the general method is acceptable now.

A new infrared, spectral radiation pyrometer devised by Strong [35a] makes possible direct steradiancy comparisons, hence normal spectral emissivity determinations in the infra-red at 8.8μ. Use is made of the residual rays obtained by successive reflections from quartz crystals. A thermocouple and attached galvanometer operate as the indicating device.

Hemispherical Spectral Emissivities by Averaging. Given for a material at some one temperature, a normal spectral emissivity, $\epsilon_{n\lambda}$, and the variation with angle of emission θ for spectral emissivities of the same wave-length $\epsilon_{\theta\lambda}$, one can compute the corresponding hemispherical spectral emissivity, $\epsilon_{h\lambda}$. By zonal integration, taking account of the fact that the projection of an element of area varies as cos θ, one obtains

$$\epsilon_{h\lambda} = \frac{\int_0^{\pi/2} \epsilon_{\theta\lambda} 2\pi \sin\theta \cos\theta d\theta}{\int_0^{\pi/2} 2\pi \sin\theta \cos\theta d\theta}. \tag{7}$$

The first precise measures of variations of $\epsilon_{\theta\lambda}$ with θ, seem to have been made by Bauer and Moulin [2] in their study of polished platinum. Similar measurements have been made by the writer, on the variations of $\epsilon_{\theta\lambda}$ for tungsten, (Fig. 1) molybdenum, tantalum and carbon. From these studies, it has been found that the ratios of $\epsilon_{h\lambda}/\epsilon_{n\lambda}$ for platinum, tungsten, molybdenum, tantalum, and carbon in order are 1.045, 1.044, 1.062, 1.042, and 0.92. While certain general conclusions seem indicated, the results are really too few in number to justify their statement.

Measurement of Total Emissivities

Method of Computation Based on $\epsilon_\lambda = f(\lambda)$. It is obvious that if $\epsilon_{n\lambda} = f(\lambda)$ is known, one may obtain ϵ_{nt} by the relation

$$\epsilon_{nt} = \frac{\int_0^\infty \epsilon_{n\lambda}\lambda^{-5}(e^{c_2/\lambda T} - 1)d\lambda}{\int_0^\infty \lambda^{-5}(e^{c_2/\lambda T} - 1)d\lambda}. \tag{8}$$

It is equally obvious that, if $\epsilon_{h\lambda} = f(\lambda)$ is known, one may obtain ϵ_{ht} in an exactly similar manner.

Drude, assuming Maxwell's electromagnetic theory, deduced the well-known relation

$$1 - r_n \quad A_1(\rho/\lambda)^{\frac{1}{2}}, \tag{9}$$

where ρ is the resistivity of the material and A_1 a constant having the value 0.365 ohm$^{-\frac{1}{2}}$. Using this relation, Aschkinass[1] derived for the total emissivity of a metal the relation

$$\epsilon_{nt} = A_2(\rho T)^{\frac{1}{2}}. \tag{10}$$

This equation was tested for platinum by Lummer[22] and by Weber.[41] Deviations were assumed to be due to the failure of the theoretical relations to take account of the variation of platinum from the Lambert cosine law.

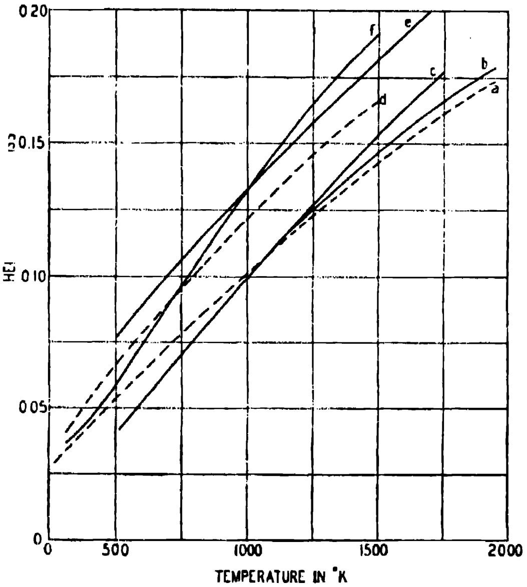

FIG. 7. A composite plot showing total emissivities, normal ϵ_{nt} and hemispherical ϵ_{ht} for platinum; (a) theoretical curve for ϵ_{nt} derived by Foote;[11] (b) curve representing average of two sets of observed values of ϵ_{nt} obtained by Foote; (c) curve representing values of ϵ_{nt} obtained by Lummer and Kurlbaum;[22b] (d) theoretical curve for ϵ_{ht} derived by Davisson and Weeks;[9] (e) curve representing observed values obtained by Geiss,[12] and separately by Lummer;[22] (f) curve representing observed values obtained by Davisson and Weeks.[9]

In 1915 Foote,[11] using the more accurate radiation constants then available, extended Aschkinass' relation to include the second-order approximation term. He obtained for platinum

$$\epsilon_{nt} = A_3(T\rho)^{\frac{1}{2}} - A_4(T\rho), \tag{11}$$

A_3 and A_4 having the values 0.5736 (ohm cm K°)$^{-\frac{1}{2}}$ and 0.1769 ohm cm K°. In the region 1000 to 1500 °K, where measurements were made, the predicted values were generally slightly too low.

Still later Davisson and Weeks,[9] taking account of the variation in $\epsilon_{\theta\lambda}$ expected in accord with electromagnetic theory, arrived at the following expression for the ϵ_{ht} for platinum

$$\epsilon_{ht} = 0.8992\,\text{ohm}^{-\frac{1}{2}}\left(\frac{T\rho}{c_2}\right)^{\frac{1}{2}} - 0.9047\,\text{ohm}^{-1}\left(\frac{T\rho}{c_2}\right)$$
$$+ 1.149\,\text{ohm}^{-\frac{3}{2}}\left(\frac{T\rho}{c_2}\right)^{\frac{3}{2}} - 1.245\,\text{ohm}^{-2}\left(\frac{T\rho}{c_2}\right), \qquad (12)$$

of which c_2 is the second radiation constant for which 1.432 cm K° was accepted. As shown in Fig. 7, computed values for ϵ_{ht} for platinum are greater than the observed values for temperatures below 700 °K, and less for temperatures above 700 °K, the difference increasing with increase in temperature. Fig. 7 also shows that both the computed and observed values for ϵ_{ht} are greater than the corresponding ϵ_{nt}. Davisson and Weeks concluded that the deviation between computed and observed results at the higher temperatures could readily be explained by the well-known failure of the Drude relation in the region of the near infrared, the visible, and the ultraviolet, evidence for which is shown in the observations for tungsten (Fig. 8).

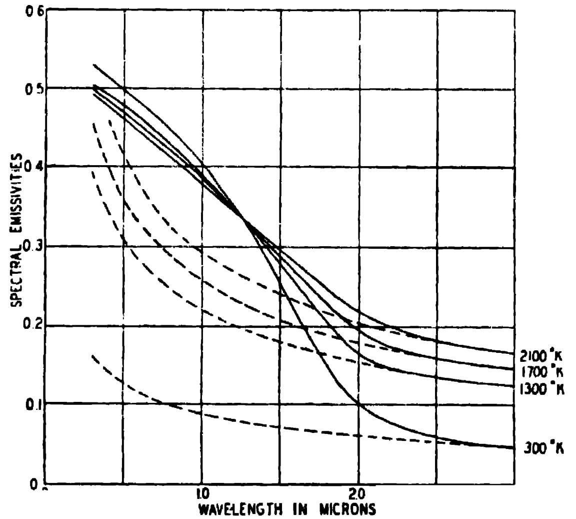

FIG. 8. Observed normal spectral emissivities for tungsten as a function of wave-length for several temperatures, and expected variations (· · ·) as a function of wave-length were the Drude relation general.

Filament in Vacuum Method. This method of measuring ϵ_{ht} is particularly applicable to metals which can be mounted and heated as incandescent lamp filaments in a vacuum. It is also applicable to substances which, in the form of thin opaque coatings, can be applied to such filaments. Temperature measurements in such instances represent the greatest sources of uncertainty.

The filament-in-vacuum method requires, for the particular temperatures concerned, that one shall be able to associate a definite heating current, and a definite potential drop with a definite length of filament whose known temperature from one end to the other is sensibly uniform. Two methods of mounting filaments for this purpose are shown in Fig. 9. In the method shown at (a), the portion of the filament chosen is that between the places of attachment of the fine potential leads. In the method shown at (b), the central portion of the longer filament is so chosen. Its length is the difference between those of the two filaments. The potential drop used is the difference between the two drops for the filaments taken separately. One has always to assure oneself by some means that the filaments are sufficiently long so that uniformity of temperature may be secured for the central portion of the longer filament.

Given a filament of length l, of circular cross-section of radius r, maintained at a uniform temperature T, by energy supplied electrically at the rate IV in an evacuated space whose dimensions are large in comparison with r and whose boundaries are at the temperature T_0, one can determine an ϵ_{ht} for the filament material at the temperature T. The condition of a steady state yields

$$IV/2\pi rl + a_{ht}'\sigma T_0^4 = \epsilon_{ht}\sigma T^4.$$

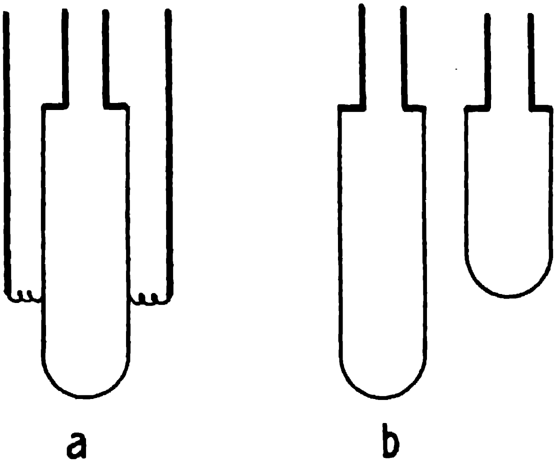

FIG. 9. Showing (a) a single filament mount with potential leads and (b) a two-filament mount with filaments of different lengths, for use in the filament-in-vacuum method of measuring ϵ_{ht}.

In order the terms represent, per unit of surface area of the filament, the rate of supply of energy to the filament electrically, the rate of supply of energy to the filament by absorption of radiant energy incident on its surface, and the rate of emission of radiant energy from the surface of the filament. It is often assumed that a_{ht}' is equal to ϵ_{ht}, but such is not the case. The radiant energy incident, since T_0, the temperature of the surroundings, will be different from T, will have a different spectral distribution from that characteristic of a blackbody at temperature T. However, if T differs but little from T_0, one may assume equality and solve for an approximate ϵ_{ht}, which later may be adjusted if additional determinations at other neighboring temperatures show that such is necessary. If, on the other hand, T is considerably in excess of T_0, the term containing a_{ht}' tends to become negligibly small and a precise value for it becomes unnecessary. In many instances that term may be neglected altogether. Generally, if not always, for metals the a_{ht}' will be less than the ϵ_{ht} for any particular case.

The foregoing method has been used considerably in determining hemispherical total emissivities of metals through wide ranges of temperature. Corresponding emittances of bodies whose surfaces are not polished, or whose partially transparent surface layers differ from the underlying layers, may be determined by this method.

Total Radiation Pyrometer Method. There are various forms of total radiation pyrometers. Which one is used is immaterial here. For this work, however, it is essential that the calibration of the instrument shall show directly or through computation the instrument response as a function of the net rate of receipt of radiant energy. If the temperature of the surroundings, T_0, is uniform, this net rate is $k(\epsilon_t\sigma T^4 - \sigma T_0{}^4)$, of which σ is the Boltzmann radiation constant and k a constant depending on the detailed dimensions of the set-up.

To obtain the ϵ_{nt} of some material at some specified temperature, T, one needs first to expose the pyrometer to the radiation from a properly prepared body of that material held at the temperature T. The body should be opaque, have a plane, polished surface oriented with its normal directed toward the pyrometer, and in size be such as to fill completely the opening in a radiation-limiting disk which is fixed with respect to the pyrometer. The instrument response, d, possibly a galvanometer deflection, is noted. Next with conditions in all respects the same, except that a blackbody also at temperature T replaces the body whose ϵ_{nt} is desired, a corresponding response, d_0, is noted. In accord with the expression for the net rate of reception of radiant energy given above, it follows that

$$\frac{d}{d_0} = \frac{\epsilon_t\sigma T^4 - \sigma T_0{}^4}{\sigma T^4 - \sigma T_0{}^4}$$

and that

$$= \frac{d}{d_0} + \left(1 - \frac{d}{d_0}\right)\left(\frac{T_0}{T}\right)^4. \qquad (14)$$

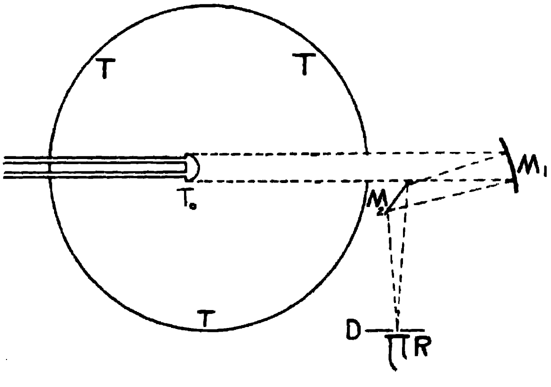

FIG. 10. Diagram of apparatus for the measurement of hemispherical total emissivities at low temperatures using the method of total reflection.

In case (T_0/T) is small compared with one or d/d_0 approximately equals one, the ratio d/d_0 may be taken as the total emissivity. If the solid angle subtended at the receiving element of the pyrometer by the aperture of the limiting disk is small, the observed ϵ_t is an ϵ_{nt}. If the solid angle is approximately hemispherical, it becomes an ϵ_{ht}. Emittances are measured by this method as well as emissivities. In industry normal total emittances are very often measured.

Method of Total Reflection. This method does not seem to have been used, though it posseses certain features tending toward precision. As shown in

Fig. 10, the material under study is shaped as a hemisphere, water-cooled to a temperature T_0, and mounted at the center of a large sphere kept at a higher temperature T. A concave mirror outside, receiving radiation from the hemisphere through a small hole in the large sphere, serves to focus the whole of the hemisphere and no more onto the blackened disk of a thermocouple receiver or a total radiation pyromter. By a slight shift of the hemisphere sidewise, the mirror, in effect, will image instead a portion of the wall on the total radiation receiver.

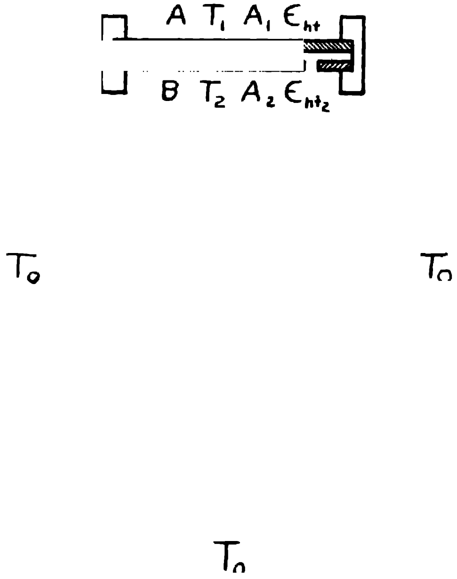
A T_1 A_1 ϵ_{ht}
B T_2 A_2 ϵ_{ht_2}
T_0
T_0
T_0

FIG. 11.

Diagram of apparatus for the parallel plate method of measuring hemispherical total emissivities.

If the receiver and its surroundings are also at temperature T_0, and if the reflectance of the hemisphere for blackbody radiation characterized by the temperature T is sensibly the same as for blackbody radiation characterized by temperature T_0, it may be shown that

$$r_{ht} = \frac{(1 - \epsilon_{ht})T^4 - T_0^4 + \epsilon_{ht}T_0^4}{T^4 - T_0^4} = 1 - \epsilon_{ht} = \frac{d}{d_0} \tag{15}$$

where d is the receiver response for the condition where the hemisphere is centrally located, and d_0 that for the condition where the hemisphere is somewhat displaced. It has been tacitly assumed that the reflectivity of the concave mirror and the absorptivity of the receiver are both unity. However, taking into account the deviations therefrom in no way affects the equality between the first and the last members of (15).

Parallel Plate Method. This method, described recently by the writer,[48] is based on the proposition that the rate of transfer of energy by radiation between two parallel plates is a function of their hemispherical total emissivities. It seems not to have been used for actual measurements, though the underlying equations are well known and have been considerably used in industry. In an opaque-walled box (Fig. 11) held at temperature T_0 and with dimensions large in comparison with those of the device contained, there is mounted an electrically heated metal plate, A, with surface kept at a temperature, T', as determined by thermocouples. Let its surface have a known hemispherical total emissivity, ϵ_{ht}, which is preferably high, and a reflectivity which is as nearly perfectly diffuse as possible. Near this plate and parallel to it on one side there is mounted a smaller circular plate, B, with one surface covered with the material to be studied and protected by a guard ring. The mass, the dimensions, and the specific heat of plate B must be known. The temperature of its surface as well as that of the guard ring must be measurable, preferably by a resistance thermometer or a thermocouple. The space between the plates and presumably inside the box should be evacuated.

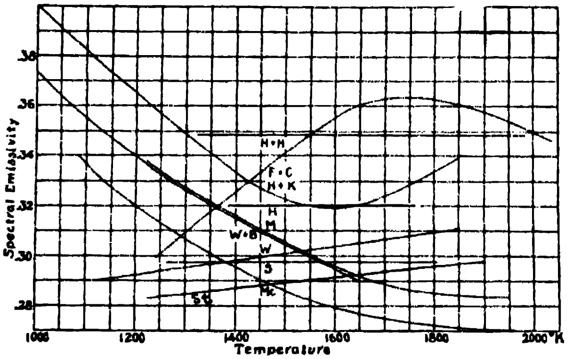

FIG. 12. Published spectral emissivities of platinum for red light at incandescent temperatures as obtained by various experimenters.

Curve	Author	Year	λ
H and *K*	Holborn and Kurlbaum [17]	1903	0.65μ
W and *B*	Waidner and Burgess [40]	1907	.66
L and *M*	Laue and Martens [20]	1907	.63
F and *C*	Fery and Cheneveau [10]	1909	.629
H	Henning [14]	1910	.665*
M	Mendenhall [28]	1911	.658
Mc	McCauley [25]	1913	.658
S	Spence [34]	1913	.658
H and *H*	Henning and Heuse [15]	1923	.647
W	Worthing [47]	1925	.665
St	Stephens [35]	1939	.665

* Interpolated from results for 0.680μ and 0.627μ.

The procedure follows. Initially by means of a cooling device not shown in the figure, plate B is brought to a temperature lower than T_0 while plate A is maintained at temperature T'. Then with the cooling device removed, one observes the temperature T of plate B as a function of time. From a plot of such data, one is able to determine the time rate $(dT/dt)_0$ at the instant that T becomes T_0. From this, the mass of the plate, its specific heat, and the area presented toward plate A, one determines the net rate of transfer per unit of area, of energy from plate A at T to plate B at T_0 by radiation. Call this rate W. Consideration of the various processes of emission, absorption and reflection between plates A and B for the above-specified characteristics for the surface of A, together with the assumption that the absorptance of B for the radiant energy incident on the A side is essentially equal to its emissivity—this would be very nearly true if T' differs but little from T_0—leads to the relations

$$W = \frac{1}{1/{}_1\epsilon_{ht} + 1/{}_2\epsilon_{ht} - 1}(\sigma T^4 - \sigma T_0^4) \tag{16}$$

and to

$$1/{}_2\epsilon_{\lambda t} = \frac{\sigma(T^4 - T_0^4)}{W} - 1/{}_1\epsilon_{\lambda t} + 1. \tag{17}$$

All the terms on the right-hand side of the equation are directly measurable. If precise measurements for the hemispherical total emissivity of a material of the corresponding emittance of a body in industry is desired the foregoing method would seem to be fairly simple and precise for the determinations.

The factor

$$\frac{1}{1/{}_1\epsilon_{\lambda t} + 1/{}_2\epsilon_{\lambda t} - 1}$$

is used in industrial calculations for the transfer of radiant energy between surfaces. McAdams[24] refers to it as an "emissivity factor."

Luminous Emissivity

This term has often been called visible emissivity. It applies to luminous radiations and can have significance only for materials raised to incandescence. An ϵ_l may obviously be obtained (1) by comparing with a photometer the brightness of the material at some temperature with that for a blackbody at the same temperature. The ratio of the two brightnesses is the ϵ_l sought. An ϵ_l may also be obtained (2) by computations based on known measured values of ϵ_λ. The formula is

$$\frac{\int_0^\infty \epsilon_\lambda L_\lambda \lambda^{-5}(e^{c_2/\lambda T} - 1)^{-1} d\lambda}{\int_0^\infty L_\lambda \lambda^{-5}(e^{c_2/\lambda T} - 1)^{-1} d\lambda}, \tag{18}$$

where L_λ is the spectral luminosity or luminosity factor of radiation. Evidently an ϵ_l is a weighted average of ϵ_λ's. To the writer's knowledge luminous emissivities have been determined only for such substances as tungsten, tantalum, and molybdenum.

Color Emissivity

Like luminous emissivity, this term can have significance only for materials at incandescence, and then only when their radiations may be color-matched with those from a blackbody at some temperature. Strictly speaking, an ϵ_c is not an emissivity at all, since radiations for the material at one temperature are compared with those for a blackbody at another temperature. It is, however, a convenient term. An ϵ_c may obviously be obtained (1) by comparing with a photometer the brightness of the material at some temperature with that of a blackbody at a temperature such that its color matches the material being studied. An ϵ_c may also be obtained (2) with the aid of an optical pyrometer whose color filter can be changed so as to yield at one time an effective wave-length λ_r, in the red, say, and at another time as desired an effective wave-length λ_b, in the blue, say. When obtaining the ϵ_c for a given material at a temperature T, one seeks for a blackbody at temperature T_c whose spectral brightness in the red bears to the corresponding spectral brightness for the material a ratio which is exactly the same as that for the blue light. This ratio is the ϵ_c sought. An ϵ_c may also be obtained (3) by computations based on known spectral emissivities for two wave-lengths in the visible, say $\epsilon_{\lambda r}$ and $\epsilon_{\lambda b}$ for wave-lengths λ_r and λ_b. For this computation it is customary to substitute the Wien spectral radiancy equation for the Planck equation. For most practical cases the error is very small. By definition

$$\epsilon_c = \frac{\epsilon_\lambda e^{-c_2/\lambda T}}{e^{-c_2/\lambda T_c}} = \epsilon_\lambda e^{-c_2/\lambda(1/T - 1/T_c)} = \text{const.} \tag{19}$$

The constant must not vary with the wave-length in the visible region. Choosing two wave-lengths λ_r and λ_b, we may write therefore

$$\epsilon_{\lambda r} e^{-c_2/\lambda_r(1/T - 1/T_c)} = \epsilon_{\lambda b} e^{-c_2/\lambda_b(1/T - 1/T_c)} \tag{20}$$

$$\ln \frac{\epsilon_{\lambda r}}{\epsilon_{\lambda b}} = c_2(1/T - 1/T_c)(1/\lambda_r - 1/\lambda_b). \tag{21}$$

For tungsten at 2500 °K, 0.665μ and 0.467μ as selected values for λ_r and λ_b, and 0.425 and 0.462 as the corresponding $\epsilon_{\lambda r}$ and $\epsilon_{\lambda b}$, we obtain with the aid of Equation (21), 2557 °K at T_c, and with the aid of Equation (19), 0.356 as ϵ_c. Color emissivities have been determined mainly for metals such as tungsten, molybdenum, and tantalum in the field of illumination.

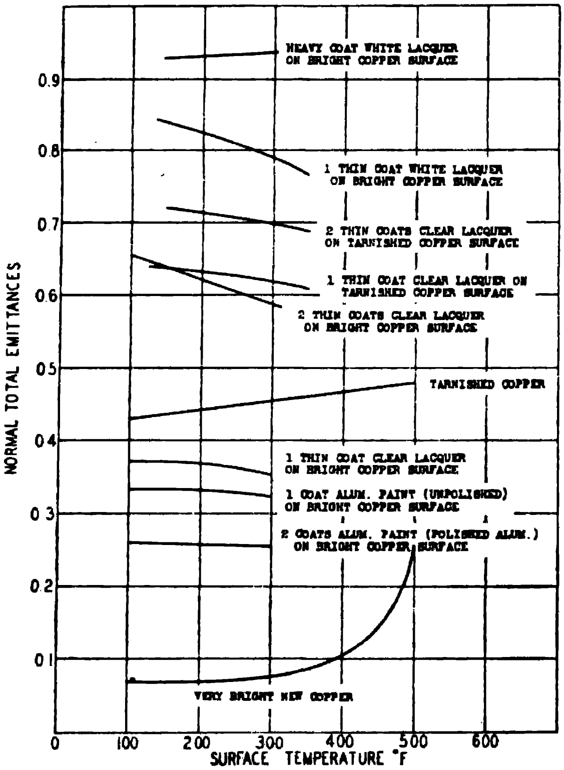

FIG. 13.

Normal total emittances at low temperatures for pieces of bright, newly polished copper when uncoated and when variously coated, as determined by R. H. Heilman.[18b]

Recently Russell[32a] has developed a color emissivity pyrometer, which compares, with the aid of photoelectric cells, spectral steradiances in the red and the blue regions. In the measurements, the precision of a null instrument is obtained by means of an electric balancing arrangement.

Measurement of Emittances

It is obvious that emittances are measured by exactly the same methods as are emissivities. There is the exception that the reflectivity methods are applicable only when the body whose emittance is being sought is opaque. This is in accord with the fact that, when the body is opaque, has a polished surface and is composed of a single material, an emittance of the body is the corresponding emissivity of the material.

When the surface of a body is polished, there is no doubt as to how one shall determine the surface area that enters into radiancy and steradiancy measurements and hence into emissivity and emittance determinations. What shall be done in the case of roughened surfaces is not so obvious. The general rule seems to be that when the roughened dimensions are small compared with distances to the receiving instruments and its dimensions, the area that is taken as source area is a projected smooth area which follows the general outline of the body. This is the case which is generally of importance. For opaque bodies, of some one material, the emittances in such cases are never less than, but instead always greater than the corresponding emissivities of the material. In some instances, as in the case of projection lamps containing crimped or —\/\/\/\—-shaped ribbon filaments of tungsten, advantage is taken of this principle to attain an emittance considerably in excess of the emissivity of the tungsten.

How the normal total emittance ϵ_{nt}' of a polished piece of copper is changed in the region of low temperatures by the addition of thin coats of lacquer, by tarnishing and by painting with aluminum, is shown by certain results obtained by Heilman [13b] (Fig. 13). For the temperatures involved, it is obvious (a) that polished copper has very low total emissivities; (b) that tarnished copper has much higher emittances than has polished copper (the increase in the very bright new copper curve in going from 300 to 500 °F is undoubtedly due to the appearance of tarnish); (c) that the total emissivities of polished aluminum are greater than those for copper; (d) that the total emittances of unpolished aluminum are greater than the corresponding emissivities; (e) that the thin coats of lacquer were not opaque; and (f) that the white lacquer when opaque is nearly black for low temperature radiations.

Emissivity Results

Spectral Emissivities. Spectral emissivities for various materials, mostly metals, are shown in Table 1. Except for a few cases where a room temperature value has been one of a group showing $\epsilon_\lambda = f(T)$, the room temperature values have been omitted. A survey of results, including much that is not in Table 1, seem to point toward certain general tendencies, though the data are too meager to really make sure in certain cases. As such tendencies we seem to have:

(1) The Drude spectral emissivity relation $\epsilon_{\lambda n} = A(\rho/\lambda)^{\frac{1}{2}}$ [Equation (9)] where ρ stands for resistivity, holds well for metals at wave-lengths beyond a rather indefinite "Drude limit" in the near infrared. (See Fig. 8.)

(2) Spectral emissivities for metals on the short wave-length side of the "Drude limit" increase with decrease in wave-length to a maximum generally in the ultraviolet. (See Fig. 8.)

(3) Spectral emissivities for metals that are not highly outgassed seem, at least in certain regions on the short wave-length side of the "Drude limit," to decrease with increase of temperature. (See Table 1.)

(4) Spectral emissivities of highly outgassed metals seem not to vary with temperature in the visible region. (See Table 1.)

(5) Spectral emissivities obtained using the tubular filament method are generally lower than those obtained by other methods. (See Table 1.)

(6) On account of deviations from the Lambert cosine law, hemispherical emissivities for metals are generally greater than corresponding normal emissivities. (See Fig. 1.)

Table 1. Normal Spectral Emissivities for Some Elements and Alloys at Temperatures Generally above 1000 °K. (Room temperature values are given in a few instances where they, along with values at higher temperatures, form a connected series and where the values given for the higher temperatures depend on those given for low temperatures.*)

Ref. No.	METHOD	T in °K	RED λ in μ, ϵ_λ		GREEN λ in μ, ϵ_λ		BLUE λ in μ, ϵ_λ		IR and UV λ in μ, ϵ_λ		REMARKS
							Carbon				
31	Tube	1600	0.66	0.89							
		2500	0.66	0.84							
							Columbium				
43	Tube	1600–2500	0.66	0.374							Highly outgassed
							Copper				
36	Spectrophotometer		0.66	0.11							Solid
	Spectrophotometer		0.66	0.15							Liquid
	Couple and pyrometer	900–2100	0.66	0.105							Solid and liquid
	Contact with Pt	1275	0.66	0.105							Solid
		1350	0.66	0.120	0.55	0.38					Solid
		1375	0.66	0.15	0.55	0.36					Liquid
	Pyrometer	1450	0.66	0.14	0.55	0.32					Liquid
	Pyrometer	1500	0.66	0.13	0.55	0.28					Liquid
							Gold				
16			0.66	0.127							
37	Spectrophotometer	<1336	0.665	0.120	0.535	0.410	0.495	0.531			Solid
	Spectrophotometer	>1336		0.208		0.405		0.473			Liquid
	Couple and pyrometer	1100–2020	0.66	0.125							Solid and liquid
	Contact with Pt	1275	0.650	0.145	0.550	0.38					Solid
	Contact with Pt	>1336	0.650	0.219	0.550	0.38					Liquid
47	Tube, reflectivity	1275	0.665	0.140	0.535	0.448	0.460	0.632			Solid
							Iron				
	Couple and pyrometer	1000	0.66	0.27							Solid
		1480–1500	0.66	0.29							Solid and liquid
	Contact with Pt	1480–1500	0.65	0.37							Solid and liquid
							Konal				
28	Pyrometer	1200	0.665	0.43							
							Molybdenum				
27	Open-V wedge	1300	0.658	0.44							
		2000		0.38							
		2750		0.39							
6		2300	0.650	0.43							
46	Tube, reflectivity, contact with tungsten	300	0.665	0.420			0.467	0.425			
		1300		0.378				0.395			
		2000		0.353				0.380			
		2750		0.332				0.365			
43	Tube	1300–2100	0.667	0.382							Highly outgassed
							Nickel				
14	Reflection										
3	Couple and pyrometer	1200	0.660	0.250							Solid
		1700	0.660	0.215							Solid
			0.660	0.215							Liquid
6	Contact with Pt	1200–1700	0.66	0.36	0.55	0.44					Solid
			0.66	0.37	0.55	0.46					Liquid
47		1200–1650	0.665	0.375	0.535	0.425	0.460	0.450			Solid
							Palladium				
40		1275	0.66	0.35							
		1725		0.31							
		1805	0.650	0.33	0.55	0.38					Solid
		1830		0.37							Liquid

							Platinum (See Fig. 12)												
							Rhodium												
43	Tube	1300–2000	0.667	0.242															Highly outgassed
							Silver												
14	Spectropyrometer		0.66	0.077															
3	Couple and pyrometer	1000–1700	0.66	0.055															Solid and liquid
6	Contact with Pt	1215	0.650	0.044															Solid
		1255		0.072															Liquid
36	Spectrophotometer		0.66	0.072															Liquid
							Tantalum												
27	Open-V wedge	1400	0.658	0.61															
		2100		0.49															
		2800		0.47															
25	Spectrobolometer	1400	0.658	0.59															
		2100		0.47															
		2800		0.46															
47	Reflectivity, tube, contact with W and Mo	300	0.665	0.493			0.467	0.565											
		1400		0.442				0.505											
		2100		0.415				0.460											
		2800		0.390															
38	Open-V wedge	1400	0.667	0.49															
		2100		0.40															
23	Tube	1200	0.665	0.459															
		2100		0.417															
		2800		0.394															
							Thorium												
43	Tube	1300–2000	0.667	0.380															Highly outgassed
							Tungsten												
29	Open-V wedge	1200	0.64	0.46															
		1700		0.48															
27	Open-V wedge	1375	0.658	0.45															
		3175		0.66															Obviously in error
6	Contact with Pt	2044	0.65	0.39															
30	Helix				0.532	0.44													
19	Helix	1400–3000	0.664	0.46	0.537	0.485													Large variations
33	Helix	1900	0.656	0.456			0.493	0.470											
	Helix	2300		0.445				0.465											
18	Photoelectric comp.	1800			0.54	0.452	0.46	0.488	0.34	0.501									
		2200				0.438		0.476		0.496									
		2800				0.424		0.465		0.492									
45	Tube	300	0.665	0.470			0.467	0.505											
		1200		0.452				0.482											
		2200		0.431				0.466											
		3200		0.411				0.452											
42, 7	Spectrobolometer Reflectivity	300							1.27	0.335	2.00	0.100	2.50	0.062					
		1300								0.335		0.162		0.129					
		1700								0.335		0.187		0.155					
		2100								0.335		0.212		0.179					
15	Cavity in sphere	2000–3200	0.647	0.49	0.536	0.49													5% uncertainty
21	Tube		0.650	0.45															
49																			
13	Reflectivity	300	.650	.453	.550	.469	.450	.492	.230	.423	.300	.505	.350	.476	.800	.466	1.000	.424	
		1200		.444		.458		.477		.411		.493		.471		.434		.388	
		2000		.436		.448		.463		.400		.483		.467		.405		.355	
39	Tube	1200–2200	.669	.46															Highly outgassed

(7) On account of deviations from the Lambert cosine law, hemispherical spectral emissivities for the semi-conductor carbon are less than for the corresponding normal spectral emissivity.

Total emissivities for various materials, as reported by Professor Hottel of Massachusetts Institute of Technology, are to be found elsewhere.[24]

There also seem to be certain general tendencies with respect to the total emissivities. Some of them are:

(1) The total emissivities of metals increase with temperature.

(2) The total emissivities of metals seem to be less than those of non-metals.

(3) The total emissivities of certain non-metals decrease with increase of temperature. (See Fig. 14.)

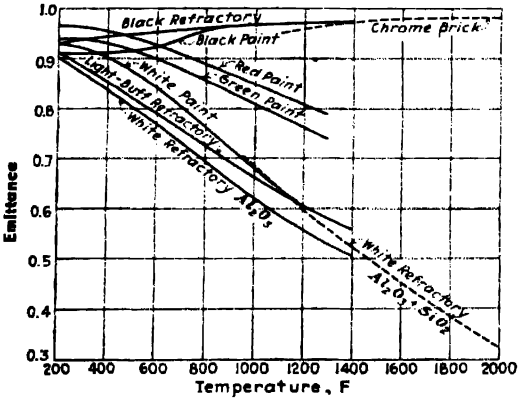

FIG. 14. Some total emittances reported by R. H. Heilman.[13a]

(4) The total emissivities of metals are generally greater than what would be expected were they to obey the Drude law. (See Fig. 8.)

(5) The appearance of a non-metal in visible light is no guide as to its probable total emissivity. (See Figs. 13 and 14.)

(6) The total hemispherical emissivities of metals on account of deviations from Lambert's law are greater than the total normal emissivities. (See Fig. 2.)

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Temperature of Incandescent Lamps

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The life and performance of an incandescent lamp depends not only upon the temperature of the filament, but also upon the temperature of the parts that are below incandescence. The operating temperature of the base determines the kind of material that can be used for sockets, and the temperature of the bulb influences the choice of material used for shades and reflectors. If the lamp bulb becomes too hot, it may soften and cause lamp failure.

It is somewhat difficult to measure the temperature of the parts of the lamp that are below incandescence because this, in general, means measuring a surface temperature, *e.g.*, of a thin piece of glass. Such measurements are usually made by the use of fine-wire resistance thermometers or by thermocouples made of very fine wire. The thermocouple method is, in general, the most satisfactory.

There are three problems to be considered in such measurements. In the first place, special efforts must be taken to see that the thermojunction reaches the temperature of the part that it is intended to measure, the danger being that the junction of the thermocouple may not be in good contact with the surface being measured, and also it may be cooled by heat conduction away from the junction, along the thermocouple wires. The first is avoided by having the junction flat and held against the surface being measured; the end loss is guarded against by using a very small wire and by holding 2 or 3 cm of the wire against the part being

Table 1. Temperature and Efficiency of General Service 115-volt Lamps.

Lamp Watts	Life (hrs)	L/W§	Temp. (°K)	Max. Bare Bulb* Temp. (°C)	Base* Temp. (°C)
6‡	1500	6.9	2400	34	31†
10‡	1500	8.2	2420	41	41
15‡	1000	9.4	2480	42	41
25‡	1000	10.5	2585	43	42
40	1000	11.9	2750	127	105
60	1000	12.9	2775	129	108
75	750	15.0	2825	136	113
100	750	16.1	2845	140	113
150	750	17.6	2875	143	109
200	750	18.5	2900	153	100
300	1000	19.2	2920	190	78
500	1000	20.3	2940	198	100
750	1000	19.4	2940		
1000	1000	21.0	3000		
1500	1000	22.	3035		
2000	1000	22.0	3050		
		Coiled Coil			
60	1000	14.0	2770	122	90
100	750	16.3	2850	127	94

*These values furnished by W. H. Fisher, Nela Park.
†Temperature at junction of base and bulb.
‡Vacuum lamps, all others are gas-filled.
§Lumens per watt.

Table 2. Temperatures of Lamps for Special Purposes.

Lamp	Volts	Current	Watts	Life (hrs)	Lumens	L/W	Temp.(°K)	Candle-power
Street Series		6.6		2000	1000	16.0	2870	
		6.6		2000	2500	17.8	2900	
		6.6		2000	4000	19.0	2935	
		6.6		2000	6000	19.2	2940	
		15.0		2000	4000	19.5	2900	
		20.0		2000	6000	20.1	2995	
		20.0		2000	10,000	20.2	3000	
		20.0		2000	15,000	20.4	3005	
		20.0		2000	25,000	20.6	3010	
CX	115		60	500		13.6	2840	
			250	500		19.0	2970	
			500	500		21.8	3030	
Airport Lighting	32		1500	100		28.0	3250	
	32		300	100		29.5	3265	
Studio or Airport Lighting	115		5000	75		29.5	3310	
	115		10,000	75		32.7	3340	
Floodlight	115		500	800		17.6	2925	
	115		1000	800		22.5	3100	
	115		1500	800		24.5	3170	
Spotlight	115		250	200		17.7	2930	
	115		400	200		20.0	3060	
	115		1000	200		22.5	3140	
	115		2000	200		25.0	3150	
			Projection Lamps					
		Area*						
Monoplane	115	151	500	200	13,250	26.5	3270	1545
	30	175	900	200	23,500	26.1	3280	2860
Biplane	115	72	500	25		24.5	3250	1700
	115	97	750	25		26.0	3355	2670
	115	135	1000	25		27.6	3360	4045
Coiled Coil								
4 seg.	115	19	50	50	790	15.8	2920	80
4 seg.	115	26	100	50	1920	19.2	2995	210
3 seg.	115	41	100	50	1850	18.5	2945	185
2 seg.	115	56	200	50	4100	20.5	3000	425
3 seg.	115	55	200	50	4240	21.2	2985	390
2 seg.	115	66	300	25	7200	24.0	3100	720
			Photographic Lamps					
Photoflood								
No. 1	115		250	2	8650		3430	
No. 2	115		500	6	16,500		3350	
R2	115		500	6			3350	
4	115		1000	10	33,500		3410	
Movieflood			2000	15	65,000		3430	
			Lamp for Type B Kodachrome					
	115		500	40	13,300		3200‡	
	115		1000	50	27,100		3200‡	
	115		1500	70	41,000		3200‡	
	115		2000	80	54,800		3200‡	
	115		5000	100	138,000		3200‡	

*Area of coil in square millimeters.

†Candlepower in direction used.

‡Color temperature.

measured. The other problems are to see that the presence of the thermocouple and necessary wires does not change the temperature of the part measured and that the thermojunction is not heated too much by the radiation from the filament. Use of fine, well-polished wire helps to overcome these difficulties. Columns 5 and 6 of Table 1 show the temperature of operation of certain lamp parts.

The temperature of the filament is, of course, the all-important characteristic of a tungsten-filament incandescent lamp. Measurement of the filament is an investigation where the disappearing-filament optical pyrometer works very satisfactorily. Since the pyrometer filament is a little over one mil in diameter, the lamp filament studied should be magnified several times so that its image, at the location of the pyrometer filament, will be considerably larger than the pyrometer filament. For measuring the temperature of lamps larger than the 100-watt, 115-volt [filament diameter 2.5 mils (.064 mm)], the objective of the optical pyrometer is a Bausch & Lomb-Zeiss-Tessar lens 2¾ inches in diameter and 12 inches in focal length. With this lens, a magnification of five to six diameters is obtained. For measuring the temperature of smaller filaments, an additional 8.5-inch focal-length Bausch & Lomb-Zeiss-Tessar lens about 1.8 inches in diameter is used. With this set-up, a magnification of about ten to fifteen diameters is obtained, and it is possible to measure the temperature of the small 6-watt, 115-volt lamp [filament diameter .5 mil (.013 mm)]. The reason that it is necessary to use a lens of such large diameter is that one cannot get close enough to the filament in a lamp to use a lens of short focal length.

Most of the lamps used for general lighting purposes have inside-frosted bulbs. Since it is necessary to see the filament when measuring the temperature, lamps to be tested must be made with clear bulbs. The bulbs have to be selected because, for large magnifications, mold marks and striae in the glass make it almost impossible to obtain accurate results. It is sometimes necessary to have special bulbs with flat windows for this work. Data on the temperature of some lamps used for general lighting purposes are shown in Table 1 and on some lamps intended for special purposes are shown in Tables 2 and 3.

Table 3. Temperature of Some Small Lamps.

Lamp	Volts	Candle-power	Watts per Spherical Candle	Temp. (°K)
Flashlight PR3	2.38	.80	1.45	2735
Flashlight PR2	3.57	1.55	1.17	2770
Flashlight 136	1.25	.19	4.10	2550
Flashlight 31	6.15	2.15	0.87	2745
Flashlight 248	2.40	1.45	1.35	2620
Flashlight 605	6.15	4.2	.88	3030
Radio Panel No. 44	6.15	.60	1.5	2400
Grain-o-Wheat surgical	1.5	.028	6.0	2115
Christmas tree	115	4.7	1.0	2625
		Lumens	L/W	
Sewing machine	115	122.	7.5	2345
Sign (clear)	115	80	8.0	2400
Photocell exciter	10	1000		3100
	10	1600		3100
	8.5	680		3200
	8	160		2660
	4	30		2935

Operating Temperatures of Vapor Lamps

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A gas or vapor in a state of discharge contains various particles each having a different velocity, and according to the kinetic theory, a different temperature. Hence an arc cannot be assigned one definite temperature value. Pirani and Rompe[1] report the temperatures in a neon discharge at 50 ma per cm[2] as follows:

Electrons	15,000 °C
Excited atoms	10,000 °C
Ionized atoms	12,000 °C
Neutral atoms and tube walls	50 °C

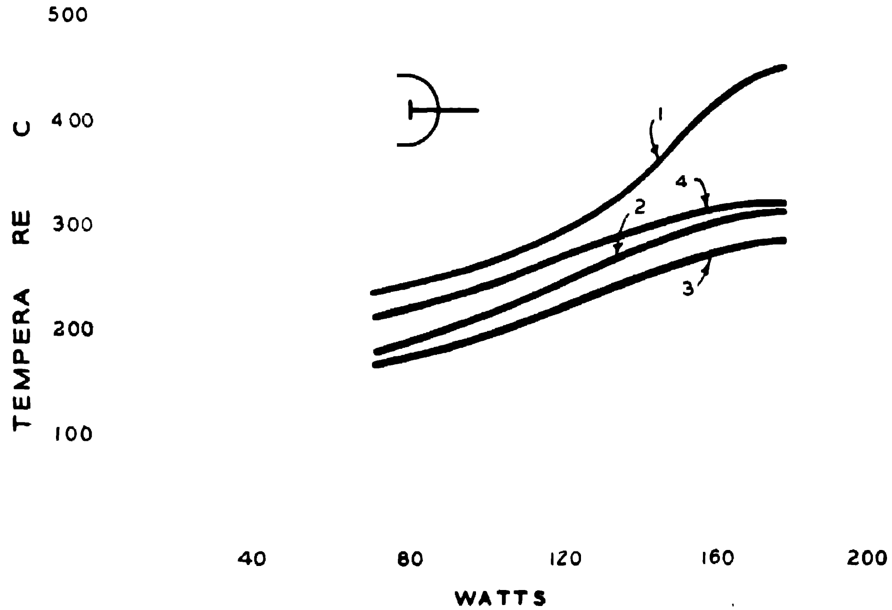

FIG. 1. Temperature distribution along walls of experimental mercury arc burned in horizontal position. Thermocouple positions are indicated. Lamp is 18 cm long, 3 cm diameter.

Although the temperature of the walls of Pirani's lamp and the neutral atoms is 50 °C, the ions may have temperatures of many thousands of degrees.

An average temperature value of a discharge has little significance where the arc stream is constricted away from the walls of the container. A commercial 400-watt mercury arc has an average temperature of 5000 or 6000 °K in the center of the arc stream[2] while the temperature near the glass walls is about 400 °C.

For the sake of simplicity and also because the temperature of the walls of a discharge tube often controls the vapor pressure, which in turn determines the electrical and luminous characteristics of an arc, it is customary to consider the wall temperature as the "operating temperature."

Determination of Operating Temperature

Low-pressure mercury discharges were immersed in water during tests covering the temperature range of 0 to nearly 100 °C. The temperature of the water was taken as the operating temperature of the lamps.[3] Higher temperatures, up to 300 or 400°, were determined by fine-wire thermocouples fastened onto various parts of the bulb, usually by kaolin and water glass. DeGroot[4] attached to an experimental high-pressure mercury-arc lamp a small-bore, closed-end manometer containing neon gas trapped behind a mercury column. The compression of the neon gas gave values for the pressures that in turn could be converted to the corresponding temperatures.

Bulb Temperature and Operating Conditions

Data on the variations of the temperature of different sections of the walls of mercury arcs with changes in operating conditions are given in graphical form in Figs. 1 and 2.

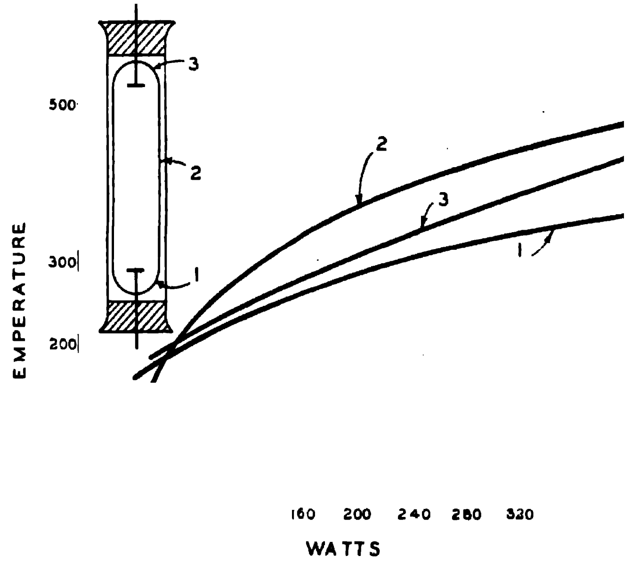

FIG. 2. Temperatures at three indicated points on walls of a mercury-arc lamp burned vertically inside a closed glass housing. Lamp of Fig. 1 in housing.

It is evident that a discharge must be carefully designed for a specified energy input and a particular operating condition, such as burning in air or in a vacuum housing, if temperature distribution over the bulb surface is approximately uniform. With a more or less uniform temperature distribution the relationship between bulb temperature and watts per cm ^{2} of bulb surface can be shown diagrammatically as in Fig. 3.

Inert Gas in Metal Vapor Lamps

Practically all vapor lamps used for illumination contain an inert gas, such as argon or neon. The inert gas facilitates starting at low voltage and also materially affects the temperatures at which low-pressure resonance radiation lamps are best operated. The effect of the inert gas on the characteristics of low-pressure lamps

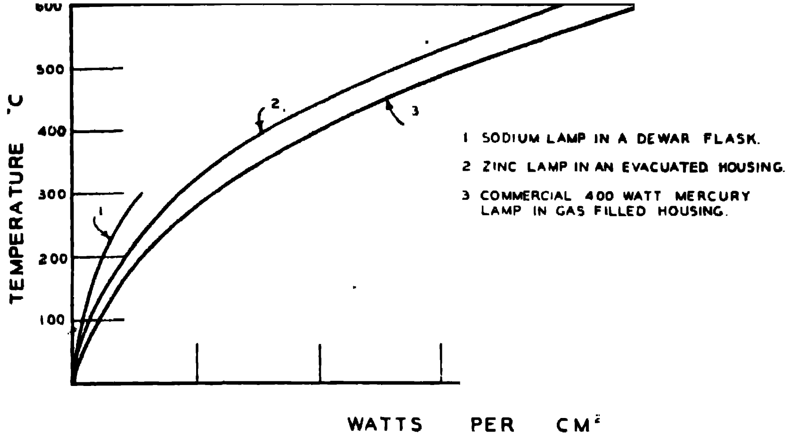

FIG. 3. Bulb temperature and watts per cm² of bulb surface for lamps burned under various operating conditions.

is in many cases the same as raising the temperature. DeGroot's data[5] are reproduced in Fig. 4 for a bulb-type sodium lamp in a vacuum housing. Neon gas materially improves the efficiency of this lamp. In a low-pressure mercury discharge the efficiency varies with the kind and pressure of inert gas, as depicted in Fig. 5. These curves show the response of a fluorescent coating, which indicates the production of resonance radiation at 2537Å. During operation the character-

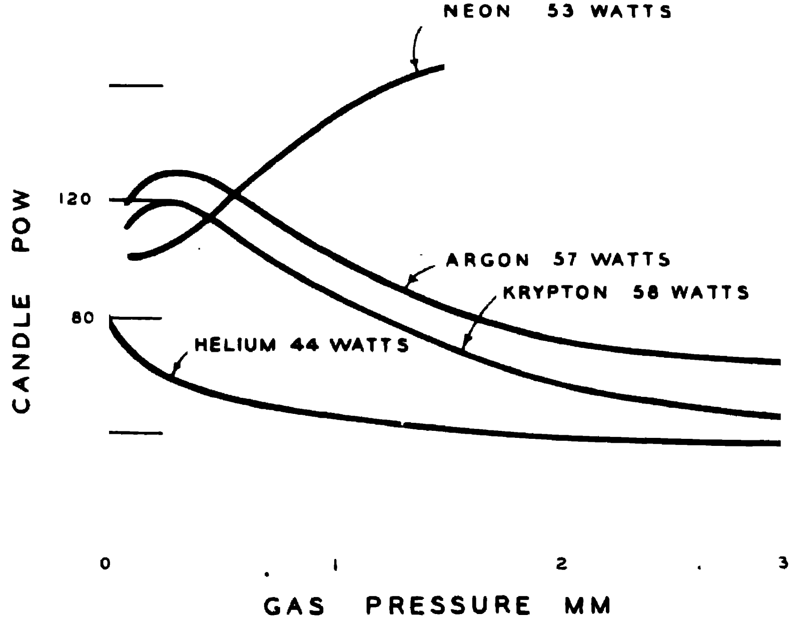

FIG. 4. Effect of inert gas pressure on light output of a sodium lamp.

istics of high-pressure discharges are not affected by the quantities of inert gas used in lamps.

Production of Maximum Amounts of 2537A Radiation

The fluorescent lamp and the Sterilamp depend upon the mercury-resonance radiation of wave-length 2537A for their operating efficiency. This particular radiation is generated most efficiently at approximately room temperature. It was discovered, however, that a pronounced decrease in efficiency occurred when mercury-resonance lamps were operated either at freezing or elevated temperatures. Immersing the lamps in water served as a simple expedient for keeping the bulb temperature constant. The data show that the intensity of both the fluorescent light and the mercury-resonance radiations are low near 0 °C, increase to a maximum between 40 and 45 °C, and then decrease again above 60 °C. If the assumption is made that the temperature of the water is the same as that of the neutral mercury-vapor atoms within the lamps, the temperature of maximum output corresponds to a vapor pressure of about 0.01 mm mercury. The relationship between temperature, vapor pressure and the mercury-resonance line at 2537A is given in Fig. 6.

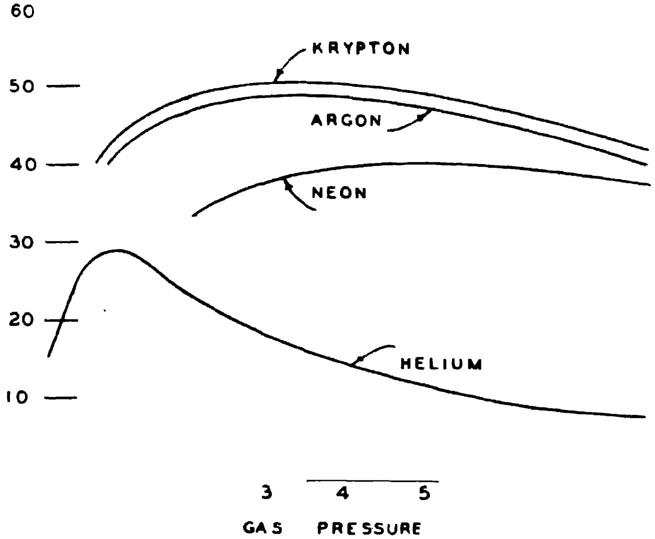

FIG. 5. Effect of inert gases at low pressures on fluorescent lamps burned at constant current.

Maximum Resonance Radiation of Sodium Vapor

Uyterhoeven and Verburg [6] state that the best operating temperature of a sodium lamp is about 240 °C, and Found [7] gives a value of 230 °C. Pirani,[8] however, operated sodium lamps of extremely high efficiency at 300 to 350 °C. According to Fonda and Young [9] the operating temperatures of sodium lamps (Fig. 7) must be controlled within reasonably close limits. The shape of the upper curve in Fig. 7 for the yellow resonance lines of sodium is very similar to the curve in Fig. 6 for the 2537A line of mercury.

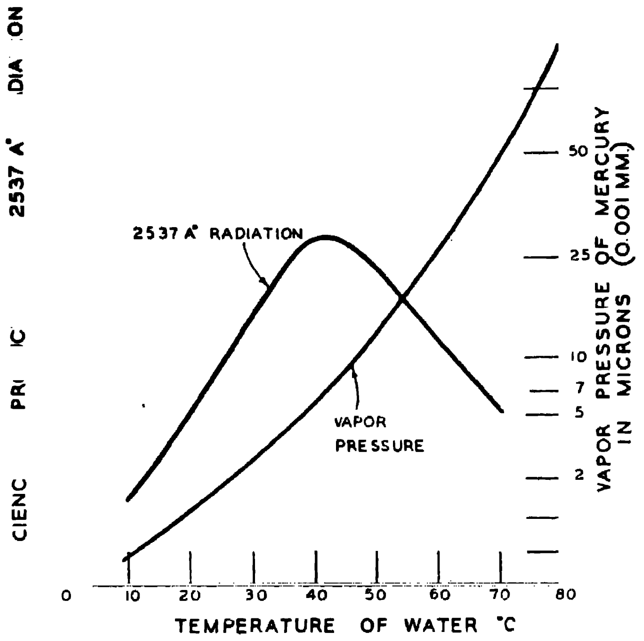

Fig. 6. Relation between temperature, vapor pressure and production of mercury 2537Å radiation.

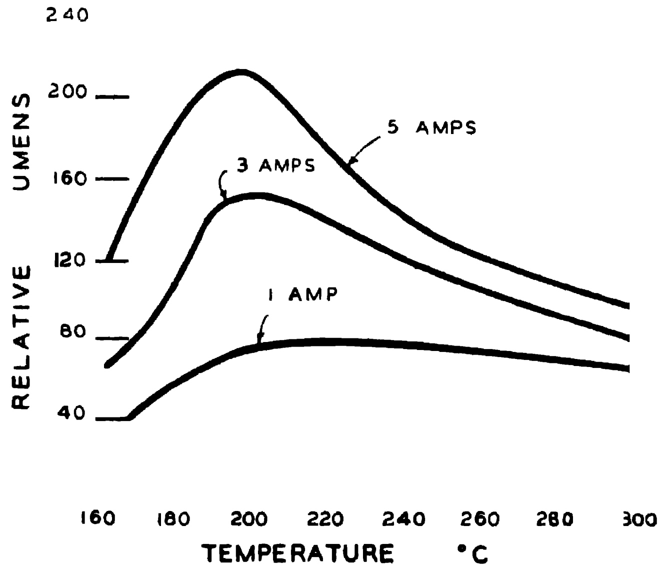

Fig. 7. Variation of luminous output with temperature of a sodium lamp.

Effect of Temperature on Spectral Distribution of Vapor Lamps

Pronounced changes occur in the radiations emitted by vapor lamps as the operating temperatures and corresponding pressures are varied. The visible light from a low-temperature, low-pressure mercury discharge is confined to a few sharp spectral lines containing only a small percentage of the radiated energy. Under such conditions approximately 50 per cent of the total energy is located in the ultraviolet resonance line of wave-length 2537Å. As the operating temperature is increased, more of the 2537Å radiation is converted into the longer wave-length ultraviolet and visible lines. With an increase of bulb temperature to 360 °C the pressure is increased to about one atmosphere and the efficiency from 4 to 40 lumens per watt. The temperature of the inner wall of the water-cooled quartz capillary arc is of the order of 800 °C and the luminous efficiency is increased to about 65 lumens per watt.

Data showing the relationship between tube diameter, operating pressure and bulb temperature for a constant-energy input of 20 watts per cm of arc stream is given in a table from Elenbaas.[10]

Table 1. Temperature of High-pressure Mercury Arcs.

Tube Diameter (mm)	Vapor Pressure (mm)	Inside Wall Temp. (°K)
40	500	600
20	1,000	740
10	2,000	905
4.5	4,000	1,060
2	10,000	1,320

According to DeGroot,[4] marked changes occur in the ultraviolet region as the operating temperature and pressure of a quartz mercury lamp is increased from a value of less than one atmosphere to 100 atmospheres. At the lowest pressures only sharp spectral lines occur, but at higher pressures and temperatures the lines become broad and fuzzy and have a continuous spectrum superimposed over them. In addition, the 2537Å line becomes an absorption line that extends to the long wave side for a distance of about 100Å at a pressure of 100 atmospheres.

Changes occur in the visible region that parallel the shifts in spectral energy distribution found in the ultraviolet, *i. e.*, broad, fuzzy lines with a superimposed continuous background. This continuous spectrum modifies the color of the mercury lamp to produce a whiter light. The mercury spectrograms in Fig. 8 show the differences between low- and high-temperature lamps.

Extremely high-temperature and -pressure mercury arcs have been described by Bol.[11] A quartz capillary lamp is surrounded by water which is circulated at a pressure of 1000 atmospheres to prevent explosion of the lamp envelope. Calculations show that the temperature on the inside wall surfaces of this lamp must be about 1300 °C. Elenbaas[12] calculated the temperature in the arc stream of a water-cooled lamp operating at a pressure of 200 atmospheres to be 8900 °K. Under these conditions the lamp has a brightness about equal to that of the sun.

Low-pressure glass cadmium- and zinc-vapor lamps are operated at a temperature of about 300 °C.[13] The vapor pressure at this temperature is only a few microns. High-pressure lamps are made with quartz envelopes to withstand a temperature of operation of about 700 °C. Some of these lamps have been operated at pressures above one atmosphere. High-temperature operation of both cadmium and zinc lamps increases the efficiency by a factor of 4 or 5 and also shifts a larger percentage of the total light into the red spectrum lines. The spectrograms in Fig. 8 show the broad, fuzzy lines radiated by these high-temperature discharges.

At low temperatures, pressures and efficiencies the light from a tellurium-vapor lamp has a continuous spectrum and approximates the spectral energy distribution of a blackbody at 6000 °K, but at higher operating temperatures the light becomes predominately yellow or gold in color. Under such conditions the spectral energy is more like that of a candle flame than a very highly heated incandescent body.[14] The tellurium arc is compared to the solar spectrum at the bottom of Fig. 8.

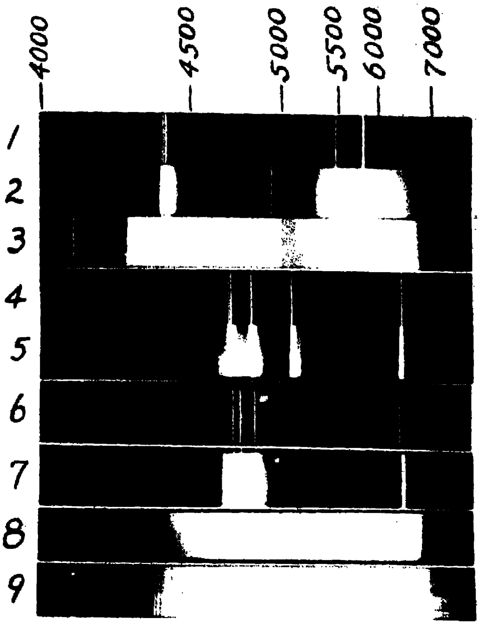

FIG. 8.

Spectrograms of various metallic vapor arcs. 1,2,3 low-, intermediate- and high-pressure mercury; 4,5 low-, high-pressure cadmium; 6,7 low-, high-pressure zinc; 8 tellurium; 9 solar spectrum.

Cesium vapor was found by Pirani[15] and his associates to give a nearly continuous spectrum throughout the visible range at a temperature of about 300 °C and a few mm pressure. Mohler[16] calculated a theoretical efficiency of the order of 180 lumens per watt for vapor pressures of 176 mm or an operating temperature of about 550 °C.

Operating Temperature Ranges of Vapor Lamps

Table 2 gives the approximate operating temperatures of commercial vapor lamps. Experimental lamps have been operated over a large range of temperatures. Low-pressure cadmium and zinc lamps are operated at about the same temperature and under the same conditions as the sodium-vapor lamp. High-pressure cadmium and zinc lamps are operated in quartz up to and even above atmospheric pressure for a short time, but such lamps have poor life.

The tellurium-vapor lamp can be operated at 100 or 200 mm pressure in quartz. Although such lamps have been operated above one atmosphere pressure, the life is only of the order a few minutes under such conditions.

Table 2. Operating Ranges of Commercial Lamps.

Mercury Lamps	Watts	Approximate Operating Temperature	Approximate Pressure
Sterilamp and Fluorescent	15–40	20–48 °C	1–10 microns
H-2 Glass	250	300	400 mm
H-1 Glass	400	360–400	1 atm
H-5 Quartz	250	470	5 atm
H-4 Quartz	100	525	10 atm
H-3 Quartz	85	590	20 atm
H-6 Quartz (water cooled)	*1000*	*785*	*100* atm
Experimental (water cooled)	*2500*	*(1300)*	*1000* atm
Sodium Lamp			
Sodium	200	220–265	0.5 to 5 microns

If some substance useful for lamp-bulb construction could be produced which would withstand higher temperatures than quartz many discharges could be operated at greater brightnesses and greater efficiencies.

Discussion

R. N. Thayer: The general shape of the light intensity curve vs. bulb wall temperature has been duplicated in similar tests.[17] A slight tendency was shown of a shift to lower optimum bulb wall temperature as current density through the arc was decreased. Thus, .5 amp through a tube of 1″ diameter showed an optimum temperature of 45 °C; at .075 amp, the optimum occurs at 36 °C.

Tubes of 1″ diameter operating at .25-.30 amp operate with the bulb wall in the optimum temperature range, for operation in still air at 25 °C. For different values of ambient temperature, of draft condition, and of lamp protection, however, bulb wall temperature varies over a wide range, and the resonance radiation and the light output of phosphors excited by it are correspondingly affected. A curve has been published[18] showing the range of light output.

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The Pyrometry of Oxide-coated Filaments

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For temperature measurements upon vacuum-tube filaments the optical pyrometer is an ideal instrument. It permits visual inspection of the filament during measurements and can be focused upon fine wires without the need of any mechanical interference. But with oxide-coated filaments special problems arise: some because of the low temperatures involved, another in obtaining the corrections necessary to convert readings into true thermodynamic temperatures.

Operating temperatures may run as low as 700 °C, while activating temperatures may be somewhat above 1,000 °C. Conventional pyrometers usually cannot collect enough light to make a filament visible in the lower range. At 700 °C a filament is barely visible in ordinary room light. A hood is necessary over the pyrometer eyepiece, and the vacuum tube must be shielded, else reflected light will be a considerable fraction of the light from the filament. We have used a pyrometer which follows in general a design by Forsythe,[1] with, however, a lens 6 cm in diameter, 15 cm focal length (f. 2.5). The images were sufficiently bright for accurate readings at 700 °C with a magnification of threefold for the image in the plane of the pyrometer lamp.

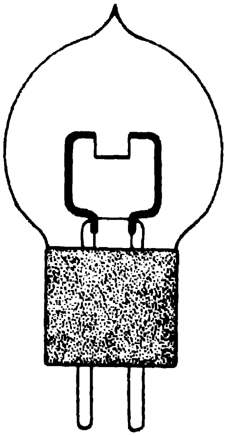

Fig. 1.
Pyrometer lamp.

This pyrometer was calibrated from 700 to 1200 °C against a standard lamp obtained from the National Bureau of Standards. A screen of Corning "Pyrometer Red" glass was used for temperatures above 800 °C. Below this temperature no screen was used, but no errors are introduced because of the predominantly red character of the light. Neither the object nor pyrometer filament has pronounced color, and they are compared at nearly the same temperature.

The conventional pyrometer lamp with a filament of tungsten wire shows a pronounced time-lag at low temperatures. This is connected with the low rate of power loss, such that an appreciable time is required to reëstablish temperature equilibrium after a change in pyrometer current. Besides the inconvenience of delay, readings will "overshoot" when a brightness match is made rapidly, while the most certain match is made when the change of contrast is fairly rapid. To obviate these difficulties we have employed a ribbon filament of platinum 80 per cent, rhodium 20 per cent, 5 mils wide by 0.5 mil thick and 0.75 inch long (Fig. 1). This construction, with its large ratio of surface to volume, minimizes the heat capacity as compared to radiation losses, so the pyrometer temperature follows changes in current with no perceptible lag. Through indirect correspondence with Dr. H. T. Wensel of the Bureau of Standards, it appears that this small cross-section obviates another source of trouble in reducing heat conduction to the support wires. Their temperature will drift about and, if heat conduction is large, may induce slow drifts in the temperature of the filament.

For work on pure metals at incandescent temperatures, the corrections to be applied to the temperatures observed directly with the optical pyrometer have best been obtained by use of the Worthing[2] blackbody. This is a hollow cylindrical filament in which fine holes are bored to permit comparison of the observed temperature of the external surface with that of the enclosure which approaches very closely the temperature of a theoretical blackbody. The properties of the oxide-coated filament however, are so variable, and depend so much upon the exact methods of preparation, that what is required is rather a ready method of measuring the spectral emissive power of filaments identical with those which may be used in actual tubes.

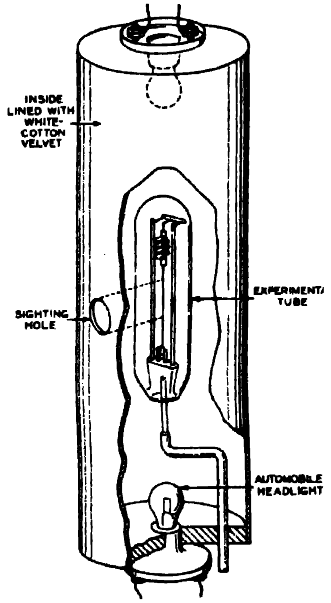

FIG. 2.
Experimental tube and reflectometer.

Such a method is provided by the measurement of diffuse reflectivity, a procedure analogous to that employed by Worthing to extend his measurements of the emissive power of tungsten down to room-temperature conditions. This depends upon the simple relation

$$\epsilon + r = 1,$$

where ϵ is the emissive power and r is the reflectivity. Because of the roughness of the coating, what is required is a diffuse reflectivity measured with light incident from all directions. To obtain these conditions the experimental tube, as shown in Fig. 2, was surrounded by a closed cylinder of white cotton velvet. At either end of this cylinder and in line with the filament were placed two automobile headlights. The optical pyrometer was sighted through a hole in the cylinder, enabling us to compare the apparent temperatures of the filament and of the back wall.

Under these conditions, with a background illumination corresponding to a brightness temperature of 1000 °C, the reflectivity may be obtained both with the filament cold and at normal operating temperatures.

The formulas used for computation are derived from the Wien radiation law which describes the spectral distribution of radiant energy from a blackbody. The reading of the back wall gives the temperature of a blackbody which would match it by substitution: *i. e.*, where T is the brightness temperature of the back wall:

$$J_1 = \frac{c_1}{\lambda^5} e^{-\frac{c2}{\lambda T}}$$

The reading of the heated and illuminated filament gives a similar brightness temperature, S.

$$\frac{c_1}{\lambda^5} e^{-\frac{c2}{\lambda S}}$$

The energy radiated by the filament is

$$J_3 = \frac{}{\lambda^5}$$

where D is the brightness temperature of the filament as it would appear with the auxiliary illumination turned off. Thus, if r is the reflectivity, and assuming the light from the walls to be scattered uniformly in all directions,

$$J_2 = rJ_1 + J_3$$

$$\frac{c_1}{\lambda^5} e^{-\frac{}{\lambda S}} = \frac{rc_1}{\lambda^5} e^{-\frac{c2}{\lambda T}}.$$

and
$$e^{\frac{c2}{\lambda}\left[\frac{1}{T} - \frac{1}{S}\right]} = e^{\frac{c2}{\lambda}\left[\frac{1}{T} - \frac{1}{D}\right.}$$

c_2 is 14330μ degrees and λ is the effective wave-length of the screen (in our case 0.66μ). The filament temperature, D, is liable to error, since it will rise when the background illumination is turned on. But up to 800 °C the total correction to r is but 10 per cent, so errors in the correction are negligible. When the filament is at room temperature the second term of the formula is negligible. For convenience in computation we have used the expression: (where $\log_{10}^{-1}$ means antilogarithm to the base 10)

$$r = \log_{10}{}^{-1}\left[-\frac{c_2 \log_{10} e}{\lambda}\frac{T-S}{TS}\right] - \log_{10}{}^{-1}\left[-\frac{c_2 \log_{10} e}{\lambda}\frac{T-D}{TD}\right]$$

Since the distribution of scattered light within the cylinder may well be non-uniform, we have checked the effect upon our measurements by the substitution of a stick of magnesium oxide in the place of the filament. This determination gave a value of 95.2 per cent for the reflectivity of this magnesium oxide. To well within the limits of our measurements this result is in agreement with the accepted value of 97 per cent.[3]

As an illustration of these methods we include measurements of a filament whose core is a five-mil wire 80 per cent platinum and 20 per cent rhodium. This core was coated with a mixture of barium, strontium and nickel carbonates which decomposed eventually to a colloidal mixture of barium oxide, strontium oxide and finely divided nickel. Activation was accomplished by glowing in methane. The final composition is shown in Table 1, where free alkaline-earth metal is expressed

Table 1. Coating Composition (Referred to Outside Surface of Coating.)

SrO = 984 μg/cm²,
BaO = 923 μg/cm²,
Ni = 71.5 μg/cm².
Active metal = 0.6–65.0 μg/cm² as Ba.

as the weight per square centimeter of the equivalent barium. The methods of analysis and the correlation between active metal and thermionic activity are described in an earlier article.[4]

Table 2. Experimental Reflectivities (%).

Tube A	μg Ba/cm²	300 °K	973 °K	1023 °K	1073 °K
Initial reading		61.0			
After bake-out		23.4			
After initial glow		32.5			
After preliminary conditioning	0.0	33.1			
Activated	19.8	36.6	38.5	36.2	37.9
De-activated	0.0	34.8	34.2	35.7	37.4
Activated	64.6	36.7	36.3	37.9	38.9
De-activated	0.0	42.4	43.1	40.9	38.9
Tube B					
Initial reading		55.0			
After bake-out		17.7			
After initial glow		32.4			
After preliminary conditioning	0.0	32.4	31.3	30.9	33.3
Activated	16.7	33.8	34.0	34.2	33.3
De-activated	0.0	31.1	32.2	33.1	33.5
Activated	37.9	34.3	32.2	33.5	35.4
De-activated	0.0	33.6	35.0	35.0	37.0

Experimental reflectivities of filaments in two tubes are shown in Table 2. For this particular type of oxide-coated filament there is no difference between reflectivity measured at room temperature and that under operating conditions. There is little if any change caused by activation, *i. e.*, formation of free alkaline-earth metal (shown as the equivalent concentration of barium). There is a gradual rise with time due to glowing, which may be caused by gradual sintering or slight loss of nickel. The most striking changes are those accompanying the decomposition of nickel carbonate (when the tube is baked out at 400 °C) and the reduction to metallic nickel, which largely takes place in the initial glow. The average of the measurements after the initial treatments is a reflectivity of 36 per cent (0.66μ) which corresponds to a spectral emissive power of 64 per cent.

Discussion

H. T. Wensel: There seems to be some misconception in regard to the question of the time required for the temperature of the filament of a pyrometer lamp to reach an equilibrium value when carrying a specified electric current. I recall pointing out the importance of conduction loss in increasing the lag, but not that the temperature will "drift about" because of end loss, if by "drifting about" is meant fluctuations not resulting from changes in ambient temperature.

In 1938 I was asked by the Editor of the *Review of Scientific Instruments* to pass upon the manuscript submitted by Prescott and Morrison.[5] I suggested that the statement "This construction, with its large ratio of surface to volume, minimizes the heat capacity as compared to radiation losses" should read "minimizes the heat conduction loss (from the central part) to the leads." Dr. Prescott replied that "in the center of the filament where there is no temperature gradient there is no loss by conduction. As I see the problem, the rate of change of temperature must be governed by such a relation as:

$$\frac{dT}{dt}=\frac{\text{power input}-\text{radiation loss}}{\text{heat capacity}}:"$$

Now that is true *if* there is no gradient; but there always is a gradient and the equation is true even approximately only when the ratio of volume to surface is small relative to the length of filament. The following is quoted from my letter of October 4, 1938, to Dr. Richtmyer, which was presumably forwarded to Dr. Prescott and is probably the "indirect correspondence" referred to:

"The ordinary Leeds and Northrup optical pyrometer lamp * is a vacuum lamp with a three-mil filament (diameter 0.0075 cm) and 3 cm long. It requires 0.33 ampere to heat the central part to 1000 °K. We have had constructed a lamp similar in all respects except that the filament was 10 cm long, the extra length being obtained by coiling the filament as shown in the following figure.

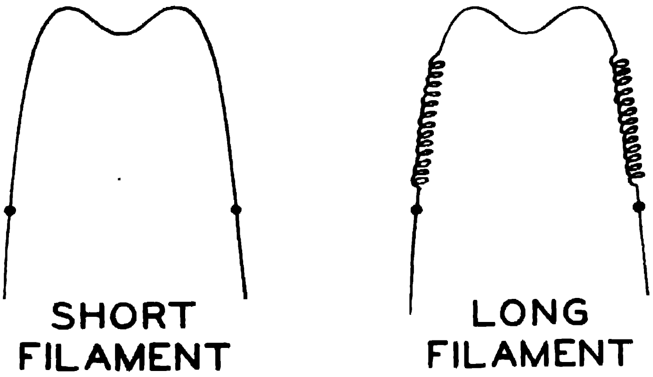

FIG. 3. Two pyrometer lamp filaments having the same diameter but different lengths.

"This lamp requires only 0.18 ampere to heat the central portion to 1000 °K. Considering a small central portion, we have in each case the same radiation loss and heat capacity, but in one case a power input over three times the other.† So that, if we assume that in the long filament $\frac{dT}{dt}=0$ (T being temperature and t being time) when the power input equals the radiation loss at 1000 °K, in the short filament $\frac{dT}{dt}=0$ when the power input is about $3\frac{1}{3}$ times the radiation loss.

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* Not the new type. The lamp in the new type has a negligible lag and no appreciable room temperature coefficient.

† At 1700 °K, where conduction loss is a small fraction of the total loss in either lamp, the two lamps require practically the same current.

The end loss is a big factor in this case. My contention can be established mathematically but it is simpler, and perhaps more convincing, to do it experimentally.

"We find that, when an ordinary L & N lamp is heated to about 1200 °K and the current is then lowered to the value (about ⅓ ampere) which will bring it to 1000 °K, it takes about 4 minutes for the middle of the filament to get within 1° of its final value. With a filament of the same size but about 3 times as long (see Fig. 1) it gets within 1° in 10 to 20 seconds. This difference can only be laid to the difference in end losses. If it were a question of heat capacity (which is the same for the two lamps), it would take longer in the case of the long filament since we are putting in much less power.

"Moreover, we find that the temperature to which the filament comes for a given current is a function of the room temperature. In the case of the ordinary L & N lamp, 1° change in room temperature causes a 3° change in the filament temperature at 1000 °K (the current being unchanged). In the case of the long filament the effect of room temperature cannot be measured. It may be about 0.1° per degree but no larger.

"Again, since it is a vacuum lamp, the effect of room temperature can be due only to end losses. Now suppose we put ⅓ of an ampere through an ordinary L & N lamp. The filament comes eventually to 1000 °K and the leads say to t_0. If now we put ½ ampere through the lamp and wait for equilibrium, at about *1600 °K, the leads will certainly warm up, say to t_0'. If now we reduce the current* back to ⅓ ampere, we must wait until the leads cool from t_0' to within ⅓° of t_0 before the filament gets within 1° of 1000 °K. That takes a long time. In the case of the long filament we do not need to wait for this, as the filament temperature is practically independent of the room temperature and hence the lead temperature (within reasonable limits). We wait only for the balance between power input and radiation loss. This is a matter of a few seconds.

"In the case of a ribbon filament lamp such as is used as a source in calibrating pyrometers, we have a filament about 3 mm wide, 3 or 4 cm long, 0.025 mm (0.001 inch) in thickness, with heavy nickel supports (leads). Here we have a large ratio [1.5 times that for the 3 mil filament and 0.5 that of Prescott's filament] of area of surface to volume (heat capacity) but the *lag* is very great. The lead conduction loss is great."

Reply

I have been glad to acknowledge Dr. Wensel's suggestion as to the importance of end loss, and to agree with his interpretation of the difference in behavior between a long and a short pyrometer filament. In contrasting our filament with his short filament, the difference in time lag is doubtless largely due to the great end loss in his filament and in accord with his interpretation.

However, the large ratio of surface to volume of a thin ribbon confers an additional advantage over a long filament, or one where end loss is minimized. In such case there is no conduction of heat from the mid-point of the filament, and the lag must depend upon heat capacity. Without exhaustive experiment we are sure that the time lags with this ribbon are far less than the 10 to 20 seconds that he quotes for his long cylindrical filament.

The calibration of Dr. Wensel's short filament depends upon room temperature. Since the thermal flow from the hot filament to the room passes through the support wires, their temperature must be the immediate factor affecting the temperature at the mid-point of the short filament. Thus it seems clear that the long time lags encountered (4 minutes) are the times necessary for the leads to drift to a steady temperature, and so establish a constant heat flow from the filament itself.

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An Improved Radiation Pyrometer*

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The new radiation pyrometer for measuring temperatures above the lower limit of visible radiation, that is described in this paper, has been designed especially to fulfill the increasingly stringent demands of modern industrial applications. Certain of its details of construction insure rapidity of response without subsequent drift or creep, substantial freedom from transient errors (caused by temporarily unbalanced temperature relations within the body of the pyrometer during a change in ambient temperature), and very small change in calibration with variation in distance factor for distances up to slightly greater than twenty times the furnace aperture. These are discussed in later pages.

A portion of this paper concerns a mathematical analysis of the temperature relations that are involved. This analysis was developed to give a clear conception of the problem as a whole and more particularly to coordinate the requirement for adequate sensitivity with the growing industrial demand for constancy of calibration when the pyrometer is operated at various fixed ambient temperatures, *i.e.*, for ambient temperature compensation.

The attainment of high sensitivity and freedom from transient errors has received a great deal of attention, as recorded by Coblentz,[1] and lately by Cartwright [2] and others, but the requirement for ambient temperature compensation was not given full consideration simultaneously. Keinath [3] reported the results of some work on ambient temperature compensation, but his treatment was too limited to satisfy the present requirements.

The diagram shown in Fig. 1 represents a lens focusing radiation from an area A_1 of a heated surface (or furnace) 1 at temperature T_1 upon a receiver 2, having area A_2 at temperature T_2, to which the hot junction of a thermocouple is attached. The cold junctions of the thermocouple are in good thermal contact with surrounding shell 3 at temperature T_3 and are assumed to have the same temperature as that of the shell.† Where a thermopile is used the area A_2 is considered to represent the part of the total receiver area that is devoted to one thermocouple.

When radiant energy falls upon a lens, only part is transmitted, the rest being absorbed or reflected. It is assumed that the lens transmits the radiant energy of all wave-lengths between 0 and λ and that within this range reflection from the lens surfaces reduces the transmitted energy to .92 times the incident energy. Use is made of values published by Holladay [4] in which he gives the proportion ϕ of the spectral energy from a blackbody within the region from ultraviolet to the limit λT with respect to the total energy radiated from a blackbody within the same period of time. Thus the lens transmits $.92\phi$ times the the blackbody radiant flux falling upon it. Subscripts to ϕ indicate the body whose temperature is used in selecting the proper value for ϕ from Holladay's table.

According to the Stefan-Boltzmann radiation law and the Lambert cosine law,[5] the radiant flux emanating from unit area of a blackbody surface at $T°K$, and passing between two conical surfaces whose elements make angles θ_a and θ_b with a line normal to the emitting surface, is

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* Not presented at the symposium.

† In this paper it is assumed that the shell or pyrometer temperature T_s and ambient temperature are equal, hence the terms will be used synonymously. Actually, the shell temperature is the important factor.

$$\begin{aligned} W_{ab} &= 2\pi J \int_{\theta_b}^{\theta_a} \sin\theta \cos\theta d\theta = \pi J \sin^2\theta \Big]_{\theta_b}^{\theta_a} \\ &= \sigma T^4 (\sin^2\theta_a - \sin^2\theta_b) \end{aligned} \tag{1}$$

where W may be expressed in watts per square centimeter of source, radiated between the cones indicated, J is the radiant intensity normal to the emitting surface, and σ is the Stefan-Boltzmann radiation constant expressed in equivalent terms.

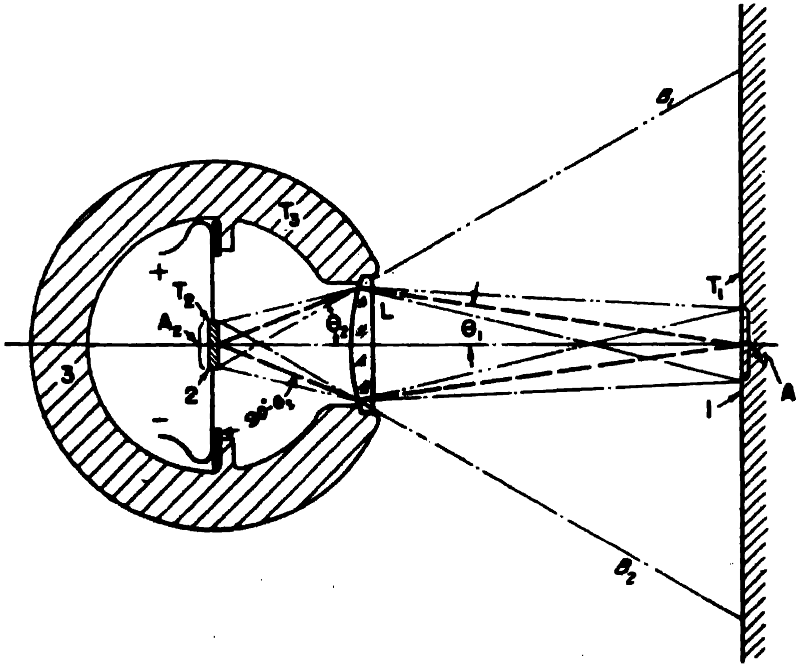

FIG. 1. Diagram used in analysis. Radiant energy from Area A_1 of body 1 at temperature T_1, focused by lens L upon body 2 having area A_2 at temperature T_2 forming receiver to which thermocouple hot junctions are attached. Cold junctions attached to surrounding shell at ambient temperature T_3. Excess temperature $T_2 - T_3$ develops thermoelectric emf.

Accordingly the radiant flux falling upon and passing through the lens from area A_1 (in which case θ_a equals θ_1, and θ_b is zero) is $.92\phi_1\sigma T_1^4\ A_1 \sin^2\theta_1$. Since $A_2 \sin^2\theta_2$ may be substituted for $A_1 \sin^2\theta_1$, this expression becomes

$$.92\phi_1\sigma T_1^4 A_2 \sin^2\theta_2 \tag{2}$$

If the front side of the receiver is a blackbody and the lens focuses all of this radiant flux upon the thermopile, expression 2 represents the radiant flux from the furnace that is absorbed by the receiver.

Likewise, expressions may be written for that radiant flux from the blackbody inner walls of shell 3 and from the lens (also at ambient temperature T_3) which is absorbed by the receiver, and for the radiant flux emanating from the receiver, the emissivity of the front surface of which is taken as unity and of the rear as e. The receiver loses heat by thermal conduction also. Equating the sum of the rates of energy absorption by the receiver to the sum of the rates of energy dissipation from it, we have:

$$\begin{aligned} &.92\phi_1\sigma T_1^4 A_2 \sin^2\theta_2 + \sigma T_3^4 A_2 (1 + e - .92\phi_3 \sin^2\theta_2) \\ &= T_2^4 A_2 (1 + e) + (T_2 - T_3)\frac{\pi}{4}\left[\frac{d_1^2 c_1 (1 + \alpha t)}{L_1} + \frac{d_2^2 c_2 (1 + \beta t)}{L_2} + G_0 (1 + \gamma t)\right] \quad (3) \end{aligned}$$

where the four major terms represent the four rates of heat exchange in the order mentioned.

By manipulation, this equation may be put into the form:

$$\frac{1 + e}{\sin^2\theta_2} T_2^4 + QT_2 = .92\phi_1 T_1^4 + M \qquad (4)$$

where

$$M = T_3^4\left(\frac{1 + e}{\sin^2\theta_2} - .92\phi_3\right) + QT_3 \qquad (5)$$

$$Q = \frac{\pi}{4\sigma A_2 \sin^2\theta_2}\left[\frac{d_1^2 c_1 (1 + \alpha t)}{L_1} + \frac{d_2^2 c_2 (1 + \beta t)}{L_2} + G_0 (1 + \gamma t)\right] \qquad (6)$$

The term Q may be called the conduction factor. Of its components as given in Equation 6, d_1 and d_2 represent the diameters of the thermocouple wires and L_1 and L_2 their lengths, all in centimeters; c_1 and c_2 are the thermal conductivities of the two wires expressed in watts per cm^2 cross-sectional area per cm length per degree C temperature difference, and G_0 represents the watts per degree temperature difference loss from the receiver by thermal conduction through the surrounding air or gas, the values of c_1, c_2 and G_0 applying for a basic temperature from which temperature change t is measured; α, β and γ represent the temperature coefficients of thermal conductivity of the materials of the two thermocouple wires and of the gas, respectively; σ, the Stefan-Boltzmann radiation constant, has the value 5.735×10^{-12} watt/(cm^{2}K$^{\circ 4}$); and A_2 is the area of the receiver in cm^2 per thermocouple. (So long as temperature is expressed in degrees K the numerical value of Q is independent of the units used for the terms in Equation 6.) When A_2 thus represents its proportionate part of the total area of the receiver the proper temperature relations are found without considering the number of thermocouples used in the thermopile. No account is taken of the heat radiated and conducted through the surrounding medium from the parts of the surfaces of the thermocouple wires not serving as receiver.

Inspection of Equations 4, 5 and 6 will show that the term Q, and none other, is dependent upon the size, shape, and materials of the thermocouples, the area A_2 of receiver per thermocouple, and the heat conducted from the receiver through the surrounding air. Consequently this term is of considerable importance in what follows. It affects the sensitivity of the thermopile, the ambient temperature errors, and the possible effectiveness of several schemes for compensating for such errors.

The proper interrelation between the several components of Q involves a separate problem that is not analyzed in this paper as it has been dealt with extensively in the published literature already referred to.[1,2] Accordingly, in what follows, the conduction factor Q, having the dimension K°^{3}, will be treated as a unit, and except as discussed later, its value will be assumed to be independent of ambient temperature.

For the numerical results of an analysis to apply accurately in practice, the effective temperature coefficient of the term Q must be taken into account, but for the purpose of providing a clear indication of the comparative virtues of widely different types of thermopiles, to serve as a guide in an experimental development of a radiation pyrometer, the present method is effective and avoids complication.

It is desirable for e, the emissivity of the rear of the receiver, to be small, and for θ_2, representing the aperture of the lens, to be large. In the design under discussion, e is assumed to be .2 and θ_2 is taken as about 12° to 13°. Accordingly $\sin^2 \theta_2$ is assigned a value .048 and $\frac{\sin^2 \theta_2}{1+e}$ is made .04. (A trial assignment of a smaller value to θ_2 leads to decidedly undesirable results from the standpoint of the present objectives.)

When the cut-off wave-length is known for the lens the values of ϕ_1 and ϕ_3 are fixed according to the choice of values for T_1 and T_3.

As indicated above, Equations 4, 5 and 6 apply for a lens transmitting all wave-lengths of radiation between 0 and λ. If a lens material is used that transmits wave-lengths between λ_a and λ_b, the corresponding values for ϕ_a and ϕ_b are taken from Holladay's table and their difference used where ϕ appears in the above mentioned equations. Two special cases will be taken up in detail: Case I applies when no lens is used, as when the source is large enough to fill the solid angle between the lines B_1 and B_2 of Fig. 1, or when a perfect mirror that fills this angle is used, and Case II applies for a fused silica lens.

Case I. When no lens is used, the terms $.92\phi_1$ and $.92\phi_3$ in Equations 4 and 5 are replaced by unity. Having angles and emissivities fixed as stated above, we assign the series of values 0, 1, 3, and 10, times 10^{10} to Q, and with a value of 300 °K (80 °F) for the shell temperature T_3, calculate the values for receiver temperature T_2 corresponding to a series of values of furnace temperature T_1 between 300 °K and 2000 °K. The value assigned for the shell temperature is then changed to 400 °K (260 °F) and other values of T_2 are calculated for the same series of values of T_1. These values are listed in columns 1, 2, and 4 of Table 1. In column 3 are listed values of ΔT_a, the excess of hot-junction temperature (receiver temperature T_2) over cold-junction temperature (shell temperature T_3) when T_3 is 300 °K. In column 5 are listed values of ΔT_b, the corresponding excess when T_3 is 400 °K. These values of excess temperature will be proportional to the emf developed by the thermopile if wires are used having a linear emf versus temperature relation. The values in column 6, giving loss in excess temperature ($\Delta T_a - \Delta T_b$) caused by heating the pyrometer body from 300 to 400 °K, are to be taken up later in connection with one type of compensation to be considered. Division of the values given in column 5 by those given in column 3 shows the fractional change in excess temperature caused by the indicated change in the pyrometer body temperature. These values, listed in column 7, are plotted and used in connection with the shunt type of compensation that is being adopted. Columns 8 and 9, which are practically self-explanatory, are considered later.

Case II. For a fused silica lens, let it be assumed that the limit of spectral transmission, λ, is 4 microns. Accordingly, values for ϕ_1 and ϕ_3 are taken from Holladay's table corresponding to λT equals four times the chosen values for T_1 and T_3, respectively. These values of ϕ are used in Equations 4 and 5, which are solved for the same sets of conditions as those specified in Case I. The results

Table 1

For Case I. With Zero Lens Absorption

1	2	3	4	5	6	7	8	9
	With Shell Temp. $T_3 = 300$ °K (80 °F)		With Shell Temp. $T_3 = 400$ °K (260 °F)					
Furnace Temperature	Receiver Temperature	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3	Receiver Temperature	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3	Loss in excess temperature caused by heating pyrometer body from 300° to 400 °K	Ratio of excess temperature with $T_3 = 400$ °K to excess temperature with $T_3 = 300$ °K	Furnace temperature required to give same excess temperature ΔT_b when $T_3 = 400$ °K as is given with furnace at temperature shown in column 1 with $T_3 = 300$ °K	Error caused by operating uncompensated pyrometer at 400 °K (260 °F) when calibrated at 300 °K (80 °F)
T_1 °K	T_2 °K	ΔT_a	T_2 °K	ΔT_b	$\Delta T_a - \Delta T_b$	$\frac{\Delta T_b}{\Delta T_a}$	T_1' °K	$T_1' - T_1$
				$Q = 0$				
300	300.00	0	397.24	−2.76	2.76	$-\infty$	400.	100.
400	306.18	6.18	400.00	0	6.18	0	516.	116.
500	318.39	18.39	405.69	5.69	12.70	.310	630.	130.
600	337.40	37.40	415.34	15.34	22.06	.411	742.	142.
700	363.07	63.07	429.98	29.98	33.09	.475	852.	152.
1000	467.52	167.52	504.10	104.10	63.42	.621	1178.	178.
1500	677.17	377.17	690.31	290.31	86.86	.770	1704.	204.
2000	897.13	597.13	902.87	502.87	94.26	.842	2216.	216.
				$Q = 1 \times 10^{10}$				
300	300.00	0	398.93	−1.07	1.07	$-\infty$	400.	100.
400	301.38	1.38	400.00	0.00	1.38	0	465.	65.
500	304.26	4.26	402.24	2.24	2.02	.526	560.	60.
600	309.47	9.47	406.28	6.28	3.19	.664	662.	62.
700	317.91	17.91	412.83	12.83	5.08	.716	767.	66.
1000	371.71	71.71	454.63	54.63	17.08	.762	1079.	79.
1500	567.11	267.11	613.51	213.51	54.60	.798	1609.	109.
2000	815.23	515.23	836.63	436.63	78.60	.847	2148.	148.
				$Q = 3 \times 10^{10}$				
300	300.00	.00	399.52	−0.48	0.48	$-\infty$	400.00	100.0
400	300.53	.53	400.00	0.00	0.53	0	460.78	60.8
500	301.66	1.66	401.01	1.01	0.65	.608	541.78	41.8
600	303.53	3.53	402.69	2.69	0.84	.762	626.7	26.7
700	307.07	7.07	405.87	5.87	1.20	.830	730.2	30.7
1000	329.94	29.94	426.29	26.29	3.65	.878	1032.8	32.8
1500	443.11	143.11	525.62	125.62	17.49	.878	1555.5	55.5
2000	670.94	370.94	724.38	324.38	46.56	.875	2097.2	97.2
				$Q = 10 \times 10^{10}$				
300	300.00	0.00	399.84	−0.16	0.16	$-\infty$	400.00	100.00
400	300.17	0.17	400.00	0.00	0.17	0	457.22	57.22
500	300.53	0.53	400.35	0.35	0.18	.650	535.12	35.12
600	301.18	1.18	400.98	0.98	0.20	.830	623.88	23.88
700	302.26	2.26	402.02	2.02	0.24	.894	718.16	18.16
1000	309.65	9.65	409.14	9.14	0.51	.947	1013.26	13.26
1500	348.87	48.87	446.81	46.81	2.06	.958	1516.37	16.37
2000	451.55	151.55	544.21	144.21	7.34	.952	2026.17	26.17

are listed in Table 2 along with derived values obtained in the same manner as the values listed in the corresponding columns of Table 1.

From the values given in Table 1, nests of curves are drawn to assist in analysis of the problem of ambient temperature compensation. No curves are presented for Case II because they would be enough like the curves plotted from the values in Table 1 for it to be sufficient to compare the values in Tables 1 and 2 to reach the required conclusions concerning Case II.

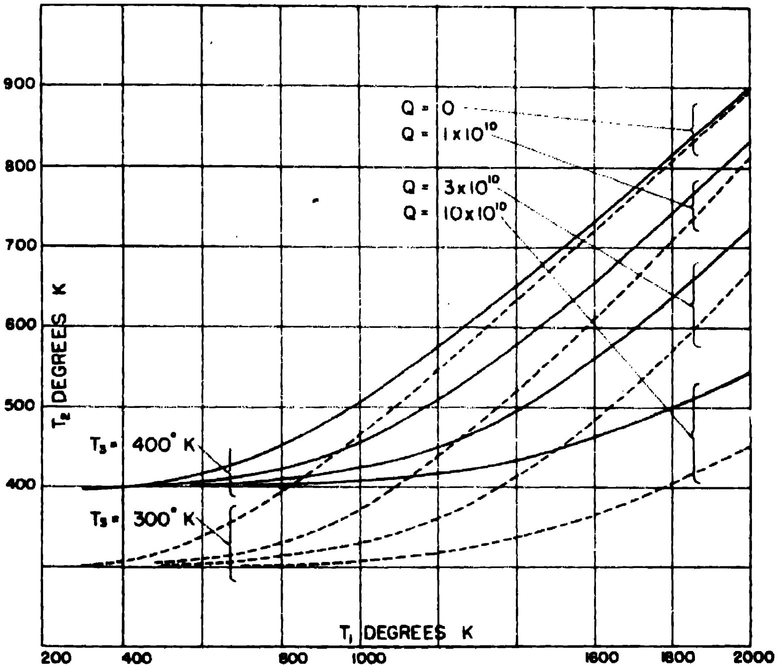

FIG. 2. Hot junction temperatures calculated according to equation 4, using ambient temperatures of 300 °K (80 °F) and 400 °K (260 °F). Plotted from values given in columns 2 and 4, Table 1 for Case I, applying for zero lens absorption. Conduction factor Q has significance given by equation 6.

In Fig. 2, the computed values for the hot-junction temperatures T_2, shown in columns 2 and 4 of Table 1, are plotted against furnace temperature T_1. The set of curves drawn in dotted lines applies when the pyrometer temperature T_3 is 300 °K (80 °F) and the solid line curves apply when T_3 is 400 °K (260 °F).

If attention is directed to the set of dotted curves alone, or to the set of solid curves alone, it will be noted that reduction in the value of the conduction factor Q leads to three characteristics:

a. It leads to greater rise in T_2 for a given value of T_1.
b. This gain in temperature rise is greatest at the relatively low values of T_1.
c. The curves tend to approach nearer to straight lines than when Q has an appreciable value.

Comparison of the family of dotted curves with the family of solid curves shows that when Q is small, a change of 100 °C in T_3 produces relatively less change in T_2 than when Q is large. That is, when the conduction factor Q is very low, the temperature of the hot junction of the thermocouple is dependent almost entirely upon the furnace temperature and relatively little upon the temperature of the pyrometer body. This is true to a greater degree with high furnace temperatures than with furnace temperatures not greatly different from that of the pyrometer body. It follows that with a low conduction factor Q, the temperature excess —the difference $T_2 - T_3$ between hot- and cold-junction temperatures—falls off to a marked extent with increase in T_3, leading to relatively large errors unless adequate compensation is possible and is provided.

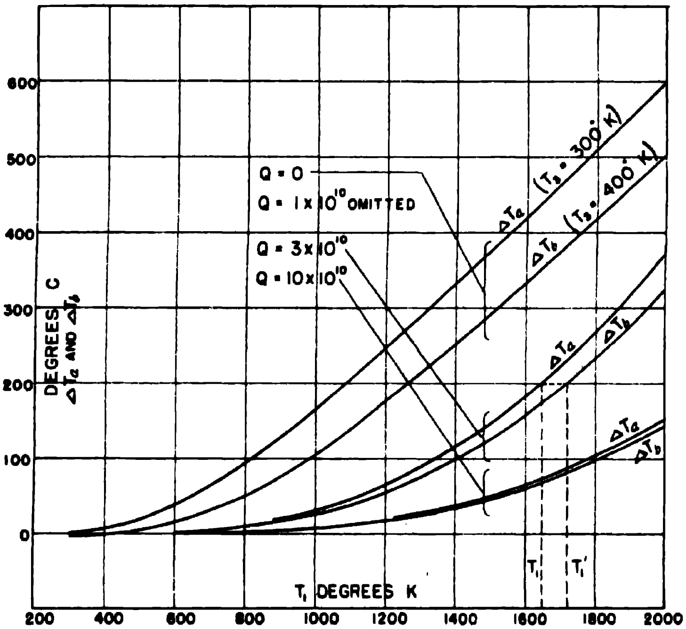

FIG. 3. Calculated excess of hot-junction temperature T_2 over cold-junction temperature T_3 obtained by subtracting respective ambient temperatures from hot-junction temperatures shown in Fig. 2. From Table 1, Columns 3 and 5.

In Fig. 3 are plotted the various computed values of temperature excess ΔT_a and ΔT_b against the corresponding values of furnace temperature T_1, as given in columns 3 and 5 of Table 1. For the sake of clearness, no curves are shown for the case where $Q = 1 \times 10^{10}$. If we assume a linear emf versus temperature relation for the thermocouples, the horizontal distances between one of the curves for ΔT_a and the corresponding curve for ΔT_b represent the ambient temperature errors caused by operating the pyrometer at an ambient temperature of 400 °K and applying a calibration made with the pyrometer at 300 °K. For example, in Fig. 3, the dotted lines show that with $Q = 3 \times 10^{10}$, a reading corresponding to a temperature excess $\Delta T = 200$ °C would correspond to a furnace temperature of $T_1' = 1720$ °K in one case and to a temperature of $T_1 = 1650$ °K *in the other.* The error would be 70 °C. Here T_1' represents the furnace temperature that would produce the same excess ΔT in hot-junction temperature T_2 above a shell temper-

Table 2

For Case II. With Fused Silica Lens

1	2	3	4	5	6	7
	With Shell Temp. T_3 = 300 °K (80 °F)		With Shell Temp. T_3 = 400 °K (260 °F)			
Furnace Temperature T_1 °K	Receiver Temperature T_2 °K	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3 ΔT_a	Receiver Temperature T_2 °K	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3 ΔT_b	Loss in excess temperature caused by heating pyrometer body from 300° to 400 °K $\Delta T_a - \Delta T_b$	Ratio of excess temperature with T_3 = 400 °K to excess temperature with T_3 = 300 °K $\frac{\Delta T_b}{\Delta T_a}$
			$Q = 0$			
400	300.152	.152	400.000	0	.152	0
450	300.534	.534	400.160	.160	.374	.300
500	301.406	1.406	400.530	.53	.876	.377
550	303.110	3.110	401.260	1.260	1.850	.405
600	306.045	6.045	402.540	2.540	3.505	.420
650	310.627	10.627	404.583	4.583	6.044	.431
700	317.058	17.058	407.700	7.700	9.358	.451
800	337.168	37.168	417.640	17.640	19.528	.475
900	365.72	65.72	433.73	33.73	31.99	.513
1000	401.02	101.02	456.33	56.33	44.69	.557
1200	483.36	183.36	518.16	118.16	65.20	.644
1500	617.94	317.94	635.70	235.70	82.24	.742
2000	841.35	541.35	853.34	453.34	88.01	.838
			$Q = 1 \times 10^{10}$			
400	300.032	.032	400.000	0	.032	0
450	300.114	.114	400.063	.063	.051	.552
500	300.300	.300	400.208	.208	.092	.691
550	300.670	.670	400.494	.494	.176	.738
600	301.322	1.322	401.000	1.000	.322	.756
650	302.365	2.365	401.814	1.814	.551	.767
700	303.972	3.972	403.050	3.050	.922	.768
800	309.394	9.394	407.246	7.246	2.148	.772
900	318.87	18.87	414.58	14.58	4.29	.772
1000	333.66	33.66	426.01	26.01	7.65	.773
1200	382.79	82.79	464.15	64.15	18.64	.775
1500	503.65	203.65	560.86	160.86	42.79	.790
2000	757.74	457.74	783.50	383.50	74.24	.838
			$Q = 3 \times 10^{10}$			
400	300.012	.012	400.000	0	.012	0
450	300.044	.044	400.028	.028	.016	.636
500	300.116	.116	400.093	.093	.023	.801
550	300.258	.258	400.222	.222	.036	.861
600	300.510	.510	400.450	.450	.060	.882
650	300.916	.916	400.818	.818	.098	.893
700	301.548	1.548	401.381	1.381	.167	.893
800	303.680	3.680	403.293	3.293	.387	.895
900	307.460	7.460	406.682	6.682	.778	.896
1000	313.501	13.501	412.089	12.089	1.412	.895
1200	334.994	34.994	431.238	31.238	3.756	.893
1500	400.14	100.14	488.59	88.59	11.55	.884
2000	611.09	311.09	671.96	271.96	39.13	.875

Table 2.—*Continued*

1	2	3	4	5	6	7
	With Shell Temp. $T_3 = 300$ °K (80 °F)		With Shell Temp. $T_3 = 400$ °K (260 °F)			
Furnace Temperature	Receiver Temperature	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3	Receiver Temperature	Excess of Hot Jct. Temperature T_2 over Cold Jct. Temp. T_3	Loss in excess temperature caused by heating pyrometer body from 300° to 400 °K	Ratio of excess temperature with $T_3 = 400$ °K to excess temperature with $T_3 = 300$ °K
T_1 °K	T_2 °K	ΔT_a	T_2 °K	ΔT_b	$\Delta T_a - \Delta T_b$	$\frac{\Delta T_b}{\Delta T_a}$
			$Q = 10 \times 10^{10}$			
400	300.004	.004	400.000	0	.004	0
450	300.014	.014	400.009	.009	.005	.643
500	300.037	.037	400.032	.032	.005	.865
550	300.083	.083	400.076	.076	.007	.916
600	300.164	.164	400.154	.154	.010	.939
650	300.295	.295	400.280	.280	.015	.949
700	300.493	.493	400.470	.470	.023	.955
800	301.173	1.173	401.128	1.128	.045	.962
900	302.382	2.382	402.294	2.294	.088	.964
1000	304.321	4.321	404.165	4.165	.156	.964
1200	311.292	11.292	410.892	10.892	.400	.964
1500	333.341	33.341	432.107	32.107	1.234	.962
2000	420.382	120.382	514.977	114.977	5.405	.958

ature of $T_3 = 400$ °K that would be produced above a shell temperature of 300 °K by a furnace temperature T_1. In like manner, other values of T_1' are determined and listed in column 8 of Table 1. The values for $T_1' - T_1$ listed in column 9 represent the error in each instance that would be caused by calibrating the pyrometer at an ambient temperature of 300 °K and using that calibration when operating the pyrometer at an ambient temperature of 400 °K. It is deemed needless to provide values corresponding to these for Table 2.

The curves in Fig. 4 show the above-mentioned ambient temperature errors computed for uncompensated pyrometers having different conduction factors. Attention is directed to the fact that with the large values of conduction factor Q, the ambient temperature errors are relatively small, while with small values of Q, the errors sometimes reach values much larger than the corresponding change in ambient temperature.

All of the curves of Fig. 4 converge at a point indicating an error of 100 °C at an indicated temperature of 300 °K. This is because the pyrometer will deliver zero emf when sighted upon a furnace whose temperature is the same as that of the pyrometer body, whatever that temperature may be.

Upon reflection, it becomes apparent that if provision could be made for Q to decrease as T_2 and T_3 increase, T_2 could be made to rise to higher values with $T_3 = 400$ °K than those represented for this condition by the curves in solid lines of Fig. 2. Such provision would serve toward compensation for ambient temperature errors. Data on temperature coefficients of thermal conductivity of metals suitable for thermocouples are scarce. Available tables show a few cases applying to some alloys where the temperature coefficients are slightly negative but not enough so to accomplish much in the way of compensation. Pure metals have rather large positive temperature coefficients of thermal conductivity, which tends to make undesirable their use for thermocouple elements.

Several methods have been used or suggested for compensating radiation pyrometers for these changes in calibration with changes in ambient temperature; *i.e.*, in the temperature of the pyrometer body. These include:

1. Use of a movable shutter carried on a bimetal strip within the pyrometer body and arranged to cut off part of the cone of heat rays reaching the thermopile receiver, the amount cut off diminishing as the pyrometer body becomes hotter. Such operation would have the effect of increasing θ_2 in Equations 4, 5 and 6, when T_8 increases.

2. Use of thermocouples[6] made of materials such that, as the temperature excess of hot junctions over cold junctions decreases with increase in T_8 and T_2, the thermoelectric power will increase in inverse proportion, thus delivering a constant emf for a given furnace temperature.

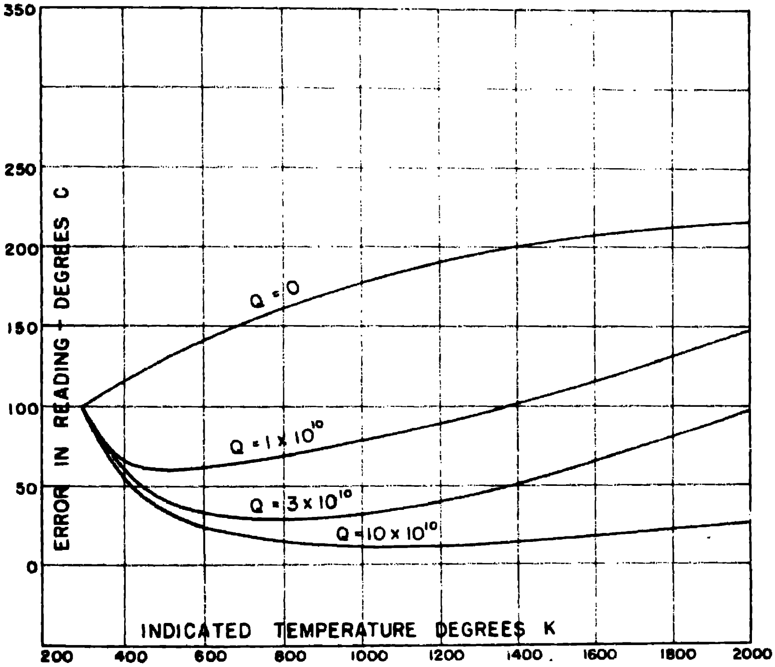

FIG. 4. Calculated errors listed in Table 1, Column 9, as produced by operating pyrometer at 400 °K and using calibration correct for pyrometer at 300 °K ambient temperature. Errors equivalent to horizontal distance between pairs of curves having same conduction factor Q shown in Fig. 3.

3. Use of thermoelectric connecting wires,[3] or "extension leads" from the pyrometer body to a point having constant temperature (or to a point at which is located other suitable compensating means such as is used in thermoelectric pyrometry).

4. Use of a shunt[3] across the terminals of the thermopile, the shunt consisting of wires of iron, nickel, or other metal having high temperature coefficient of resistance. A variation of this is the use of a resistance having negative coefficient in series with the thermopile, with a fixed shunt.

It was decided to eliminate method (1) unless it should be found that none of the alternatives could be used. This was because of the manufacturing inconvenience of having moving parts within the pyrometer and of making proper adjustment to these parts for correct compensation. Method (2) does not offer much promise on account of the present lack of suitable materials—those giving a usable thermoelectric power at low thermocouple temperatures with the proper rate of increase with increase in temperature. This leaves methods (3) and (4) to be considered.

In method (3), if extension leads are used to connect the pyrometer terminals to a point at a fixed temperature of, say, 300 °K, these leads will contribute no emf to the circuit when the pyrometer body also is at 300 °K. If the pyrometer body is then heated up to 400 °K, the extension leads will contribute a given emf, depending upon the nature of the leads and not upon furnace temperature. This emf will be added to that developed by the thermopile. By choosing suitable extension lead wire materials, this added emf can be made equal to the loss by the thermopile corresponding to any one selected furnace temperature, say, $T_1 = 1000$ °K. At this temperature, the extension leads should make up for the loss in excess temperature, $\Delta T_a - \Delta T_b$, as shown in columns 6 of Tables 1 and 2. Since the values of loss in excess temperature differ for different furnace temperatures, this type of compensation could not hold at all closely over an extended range of furnace temperatures. Accordingly, this method of compensation is eliminated from further consideration.

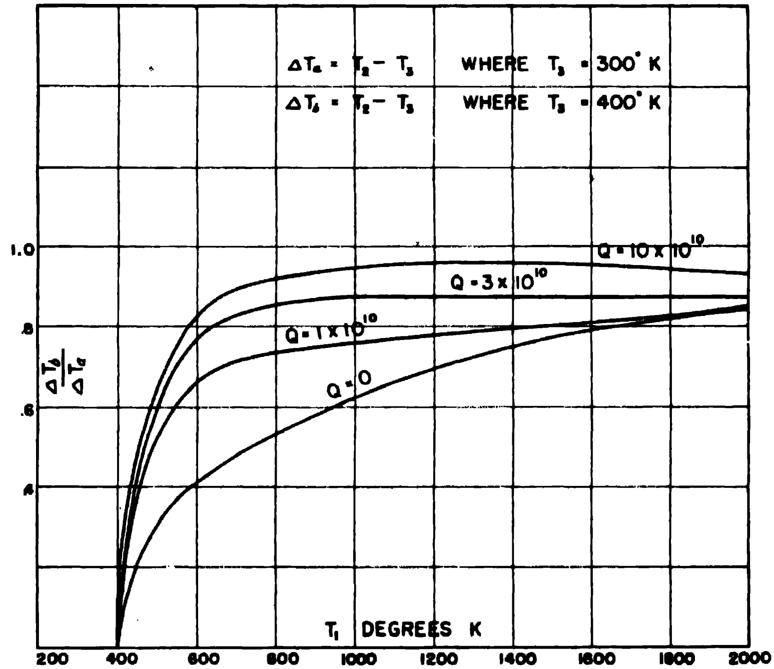

Fig. 5. Computed ratios of excess temperature ΔT_b for ambient temperature T_3 equals 400 °K to corresponding excess temperature ΔT_a for $T_3 = 300$ °K applying for same furnace temperature T_1 °K. Plotted from Column 7, Table 1. Horizontal part of curve for $Q = 3 \times 10^{10}$ indicates best condition for compensation by nickel shunt across thermopile terminals. As in Figs. 2, 3, and 4, this applies for Case I with zero lens absorption.

In compensation method (4) a coil of nickel wire is mounted within the pyrometer body and connected as a shunt across the thermopile terminals. It should be so mounted as to insure its being always at the temperature of the cold junctions of the thermocouples whether the pyrometer temperature is steady or changing. The potential drop across the coil will be a variable fraction of the emf of the thermopile, the fraction increasing as the coil heats. This increase compensates for the loss in thermopile emf that accompanies the heating of the pyrometer body. With thermocouple wires of substantially zero temperature coefficient of resistance, the fractions mentioned will be independent of the temperature T_2 of the hot junctions and hence independent of furnace temperature T_1. Assuming a linear emf versus temperature relation for the thermocouple wires, such a shunt can provide proper ambient temperature compensation when $\Delta T_b/\Delta T_a$ is constant for all the values of furnace temperature T_1 to be measured.

Reference to Fig. 5, plotted from the computed values given in column 7, Table 1, will show that this requirement is most nearly fulfilled in the case where $Q = 3 \times 10^{10}$, for which the value of $\Delta T_b/\Delta T_a$ is between .878 and .875 for all values of T_1 from 1000 to 2000 °K. Thus, if a pyrometer is designed with a conduction factor of about this value, it lends itself to compensation by the nickel shunt method, and such compensation will provide good accuracy of compensation for a wide range of industrial conditions.

For Case II, applying for a fused silica lens, the computed values given in column 7 of Table 2 indicate that the choice of a value for Q lying between 3×10^{10} and 10×10^{10} should most closely fulfill the requirement for constancy of the ratio $\Delta T_b/\Delta T_a$ throughout the operating range.

The assumption that Q does not change with varying ambient temperature, which has been applied in computing the foregoing tables, is usually not strictly accurate. In Equation 6, temperature coefficients α, β and γ usually are positive, wherefore an increase in ambient temperature produces an increase in the value of Q. This leads to greater loss in sensitivity with a given increase in ambient temperature than that indicated in columns 7 of Tables 1 and 2. In turn proportionately greater shunt compensation is required. To investigate this condition, values of ΔT_b determined for the higher value of Q would be divided by values of ΔT_a applying for the lower value of Q. No mathematical treatment of this phase of the problem is undertaken in this paper. The findings covered thus far were used as a qualitative guide to a rather intensive experimental study in which the finer refinements of operating characteristics were worked out for the instrument being designed.

The guide posts clearly apparent from this mathematical analysis are that thermopiles designed for the maximum sensitivity are subject to the greatest ambient temperature errors and these errors are the least susceptible to compensation; a thermopile having a large conduction factor has smaller errors which for such furnace temperatures as are here involved, may be compensated very satisfactorily by means of a nickel shunt across the thermopile terminals.

The foregoing considerations indicate the reasons for the adoption of a pyrometer having a thermopile with a fairly high conduction factor provided with a nickel resistance shunt in order to obtain the best ambient temperature compensation. With a high conduction factor thus being decided upon, it becomes apparent that it is more desirable, on the whole, to mount the thermocouple in air rather than in an evacuated chamber, since the latter exhibits relatively little advantage theoretically, and considerable disadvantage structually, when Q is to be made large.

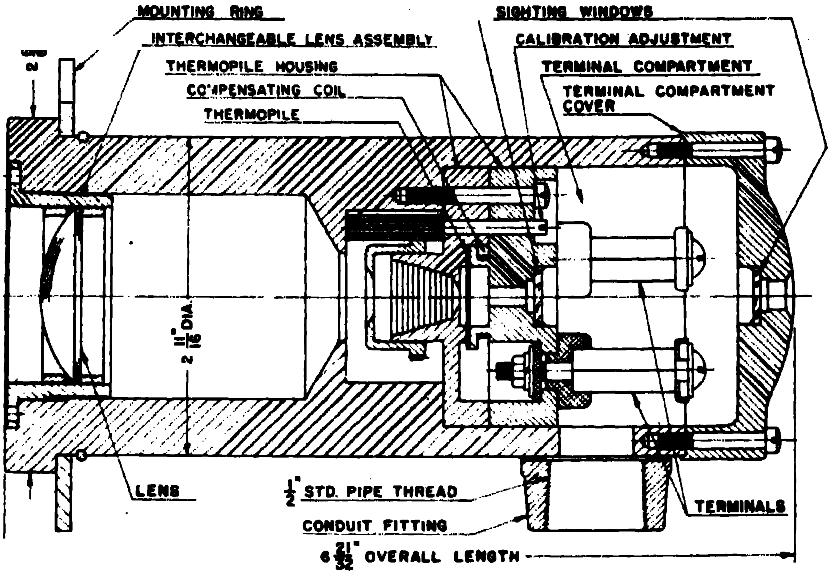

FIG. 6. Cross-sectional view of new radiation pyrometer.

Fig. 6 shows a cross-sectional view of the pyrometer that has been designed to fulfill the five requirements stated at the beginning of this article. It is intended for measuring temperatures from the lower limit of visible radiation up to the highest encountered in industrial processes.

At the left is a lens, in the center a sub-housing containing the thermopile and ambient temperature compensator, and at the right, the terminal compartment with

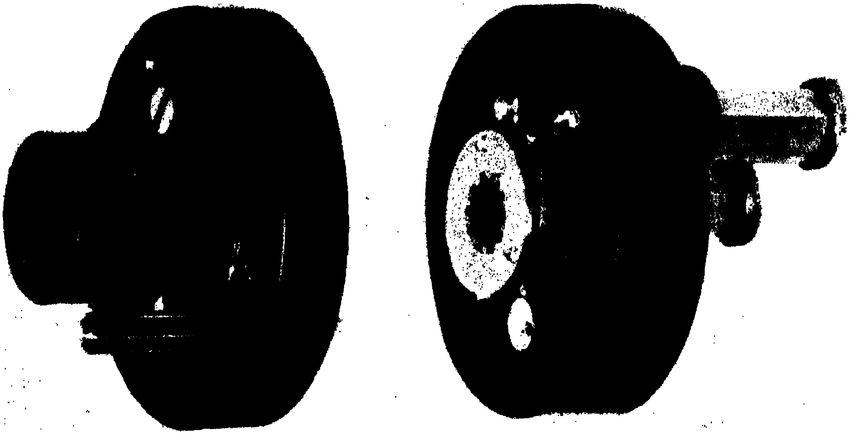

FIG. 7. View of opened thermopile housing showing calibrating diaphragm on left-hand part, and thermopile and shunt coil for ambient temperature compensation facing inward. About 2¼" O.D.

its binding posts, conduit fitting and cover. A mounting flange is shown at the front end of the pyrometer.

To obtain the distance factor of 20 : 1, the angle of view has been maintained at about 2.9° while reflections are prevented from reaching the sensitive elements. The lens concentrates radiant energy upon the hot junctions through a field-limiting aperture in the sub-housing immediately in front of the thermopile.

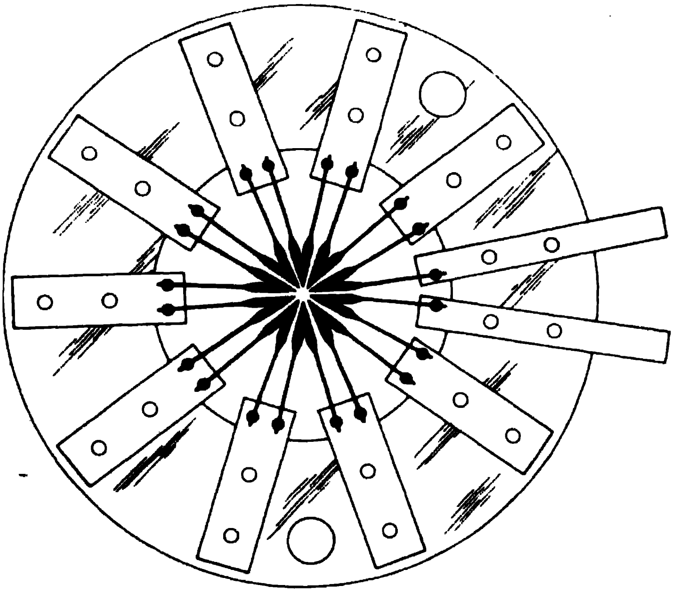

FIG. 8. Enlarged view of thermopile showing hot junctions flattened to form receiver, and terminal strips staked to annular ring of mica. Spot-welded throughout to withstand elevated temperatures. About .870" O.D.

In Fig. 7 appears a view of the thermopile housing showing its adjustable calibrating diaphragm. This unit has been opened to picture the thermopile, and the compensating shunt winding so located as to insure thermal equality with the housing at all times. In the factory and for certain field applications, the sensitivity may be adjusted by screwing the calibrating diaphragm in or out by means of a pinion whose slotted stem (usually sealed) is reached with a screwdriver through the terminal compartment.

Sealed windows in the thermopile housing and the back cover plate facilitate sighting the instrument upon any desired object.

Fig. 8 shows a view of the thermopile enlarged in relation to the other parts. It consists of ten V-shaped thermocouples spot-welded to a terminal assembly consisting of thin flat strips of metal attached at evenly spaced intervals to an annular disc of mica. The flattened "hot junctions" of the thermocouples are spaced around the center of the disc and form the radiation receiver, which is blackened on the front side to absorb the incident radiation.

The cold junctions of the thermocouples are located at the points of attachment to the metal strips. The thermopile terminal assembly, sandwiched between two other annular mica discs for electrical insulation, is clamped between the front

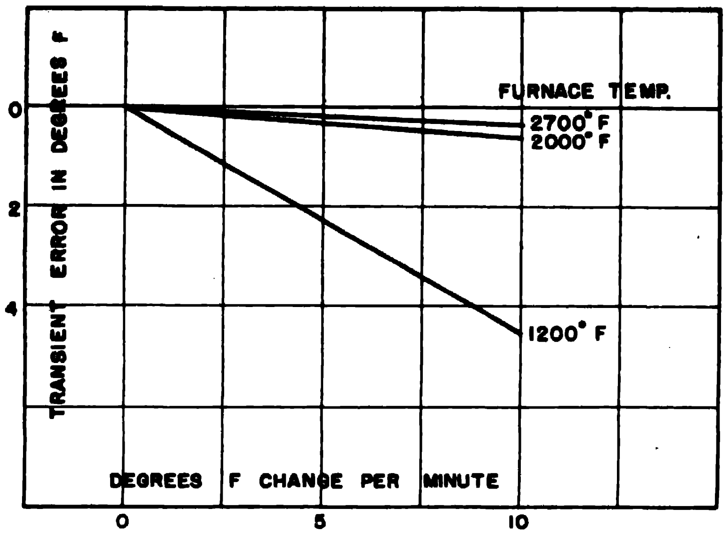

Fig. 9. Observed transient errors caused by temporarily unbalanced temperature conditions during time of changing ambient temperature. Seen to be practically insignificant for reasonable conditions.

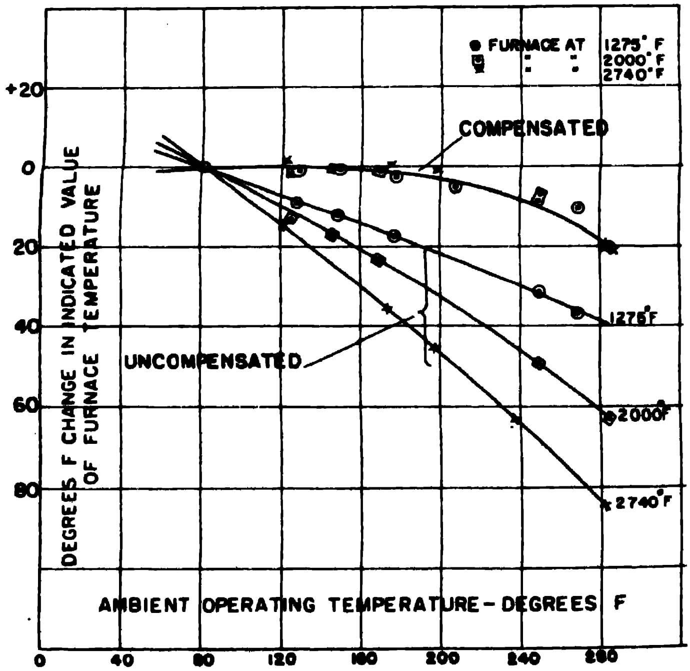

Fig. 10. Observed ambient temperature errors. The upper curve applies for pyrometer as manufactured, with nickel shunt ambient temperature compensator. Lower curves apply for the same instrument with the shunt circuit opened to remove compensation. Pyrometers having thermopile with much smaller conduction factor Q (equation 6) would have considerably greater errors, as shown in Fig. 4.

and rear parts of the thermopile housing, these parts being drawn into contact with each other over the large surface area outside of the thermopile. The parts of the housing are made thick to insure temperature equality throughout their mass. The thin flat cold junction strips, which have very low heat capacity, are exposed to the housing parts over relatively large areas through thin sheets of mica in order to insure continuous temperature equality between them and the housing. The chamber within the housing, in which the thermopile is located, is small enough to eliminate convection air currents and to minimize the time required for the contained air to assume a state of equilibrium with respect to the housing.

Table 3.

Furnace Temperature T_1 °K	Values of excess of receiver temperature T_2 over shell temperature at T_3 = 300 °K	
	Observed Values of ΔT_a (°C)	Calculated Values (°C) of ΔT_a using fused silica lens, when conduction factor Q equals 10×10^{10}
650	.3	.295
700	.5	.493
800	1.2	1.175
900	2.4	2.382
1000	4.5	4.321
1200	12.1	11.292
1500	34.8	33.341
1750	73.3	67.297

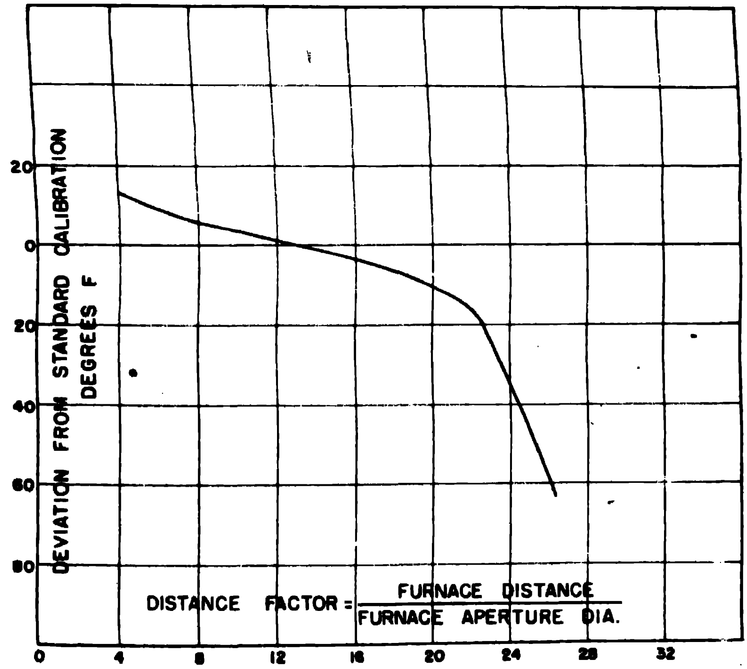

Fig. 11. Average curve of observed change in reading with change in distance factor, or ratio of furnace distance to furnace aperture diameter, without outer baffles and without readjustment of sensitivity. Not much variation was noted for all furnace temperatures within range of instrument.

In conjunction with the foregoing, the use of relatively short thermocouple wires, chosen to provide the proper conduction factor, and the absence of any extra metal disc for use as a radiation receiver combine to insure that the hot junctions as well as the cold junctions of the thermopile will respond completely to changes in the housing temperature with such rapidity that transient errors are made negligible.

The curves shown in Fig. 9 are drawn from test data giving the transient errors in temperature measurement produced when the pyrometer body temperature varies at the indicated rates in degrees F per minute. A change of 10 °F a minute is of course extreme, but even at such a rate, the temperature errors can be seen to be amply small even at comparatively low values of furnace temperatures.

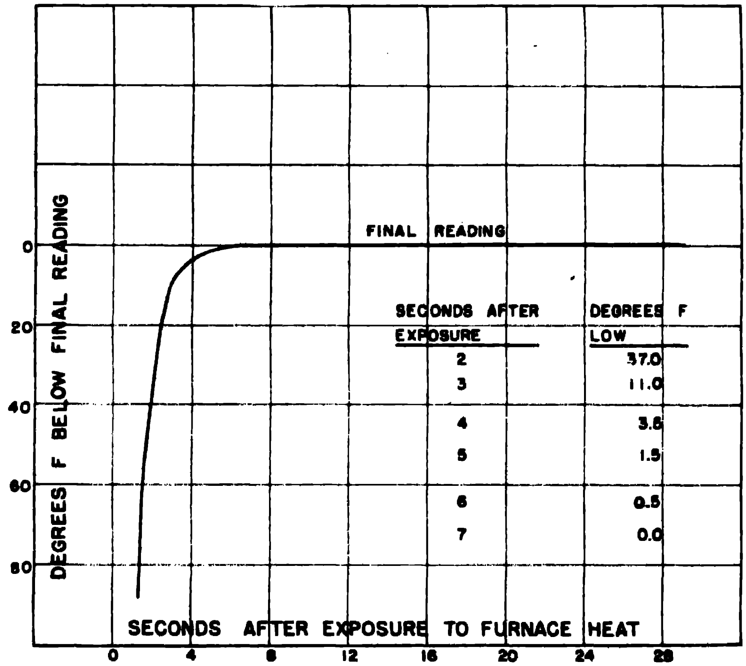

FIG. 12. Composite curve showing observed rate of response of pyrometer when suddenly exposed to hot furnace. Applies almost within width of line for temperatures from 1200 to 2750 °F.

Table 3 gives a list of observed values of excess temperature of the receiver over the pyrometer temperature, in comparison with the computed values shown in Table 2, column 3, for the same ambient temperature, the value $Q = 10 \times 10^{10}$ being chosen for this comparison. The close agreement between observed and computed values of excess receiver temperature indicates that the pyrometer as developed has a conduction factor Q whose value is a little less than 10×10^{10}. Inspection of the values listed in column 7 of Table 2 shows such a conduction factor to be very favorable for good ambient temperature compensation when a fused silica lens is used.

Fig. 10 shows curves representing ambient temperature coefficient tests taken on the new pyrometer both with and without the compensating shunt being connected.

The three lower curves apply for the pyrometer when uncompensated. These show the errors in degrees Fahrenheit corresponding to furnace temperatures of 1275 °F, 2000 °F, and 2740 °F. The single upper curve represents the corresponding errors when the nickel shunt is connected across the terminals of the thermopile.

If it is desired to raise the right-hand end of the upper curve while preserving zero error at 80 °F, this can be done by decreasing the resistance of the shunt. Points between 120 and 160 °F will then be thrown slightly above the line representing zero error.

Fig. 11 shows the way in which the observed pyrometer indication varies with respect to variation of distance factor. This curve applies when the pyrometer is sighted upon the furnace aperture without any intervening baffles or diaphragms, and without making any adjustments in sensitivity or focus beyond the initial factory setting. The curve is a composite of three sets of data, and it holds reasonably closely for all furnace temperatures at which tests were made (1200 to 2750 °F). The appearance of this curve suggests somewhat large deviations of readings with respect to furnace ratio, but close examination will show that the deviations are rather small. Considerable care was given to problems such as those of providing the best focus, aperture construction and spacing, and internal stray ray baffles, in order to make the instrument as independent as possible of distance factor variations within wide limits.

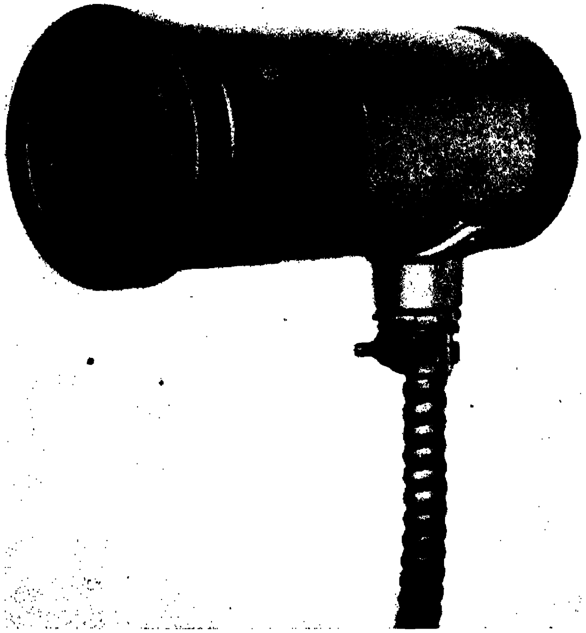

FIG. 13. View of finished pyrometer showing mounting flange at left, and at right, the terminal compartment cover and detachable conduit fitting.

Fig. 12 gives the observed time for response. If the pyrometer is sighted upon a furnace aperture and then has its lens covered for any chosen length of time, the response upon removal of the cover from the lens will be as shown. This curve is substantially exact for any furnace temperature from 1200 to 2700 °F. The upper edge of the curve corresponds more closely to the rate when the furnace is at 1200 °F and the lower edge when the furnace is at 2700 °F. The reading, in terms of furnace temperature, comes within 3.5 °F of a stable value in four seconds, within one-half of a degree or less in six seconds, and at the end of seven seconds the reading has reached a final value from which it does not depart as long as the furnace temperature remains constant.

Fig. 13 shows a view of the complete radiation pyrometer. A mounting flange provided at the front adapts the instrument for use with any one of a group of accessories suited to various industrial applications. This instrument is believed to meet industrial needs that are continually expanding and at the same time becoming more critical in their demands.

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Chapter 13

Thermometric Metals and Alloys

Electromotive Force of Alloys in Various Alloy Systems

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Polytechnic Institute, Troy, N. Y.

The physical properties of a number of alloys in various alloy systems have been investigated in recent years. While the information in these researches dealt in the main with the electrical resistance and resistance to oxidation at high temperatures, a considerable amount of information on the electromotive force of these alloys has been obtained. This information is abstracted in the tables which follow. To avoid inclusion of a large amount of tabular data only the electromotive force at 1000 °C is given. The linearity of the electromotive force in relation to temperature can be determined from the graphs which accompany each table. All values for electromotive force are related to platinum with cold junction 25 °C.

Table 1. Nickel-Chromium Alloys.[1]

Alloy No.	Composition				Emf at 1000 °C (mv)
	Ni	Cr	Mn	C	
R 1	99.6	0	0.4	...	-12.55
R 2	97.6	2	0.4	...	+15.19
R 3	94.6	5	0.4	...	+27.87
R 4	89.6	10	0.4	...	+31.27
R 5	84.6	15	0.4	...	+27.07
R 6	79.6	20	0.4	...	+22.30
H 3	94.0	5.0	1.0	...	+26.18
H 1	92.49	6.45	0.88	0.18	+29.89
H 2	89.81	8.70	1.30	0.19	+29.69
H 4	89.34	9.55	0.95	0.16	+29.06

This system includes the well-known alloy, Chromel, used extensively in thermocouples today. The emf of alloys in this system becomes increasingly positive to platinum until an addition of about 8.5 per cent of chromium has been made. Further additions of chromium lower the emf of the alloy. Alloys of the 80-20 class, while superior in resistance to oxidation at 1000 °C, have somewhat lower emfs (Figs. 1, 1A).

Table 2. Nickel-Molybdenum Alloys.[2]

Composition		Emf at 1000 °C (mv)
Mo	Mn	
5	1	6.3
10	1	28.3
16	1	34.8
20	1	40.0
20	3	28.5
20	5	29.7
25	1	37.9
30	1	37.4

The emf of nickel-molybdenum alloys becomes increasingly positive to platinum with increasing additions of molybdenum until 20 per cent of molybdenum has been added. With higher percentages the emf decreases again. The maximum emf

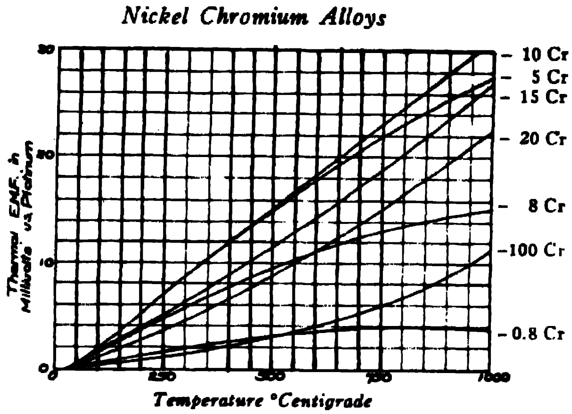

FIG. 1.

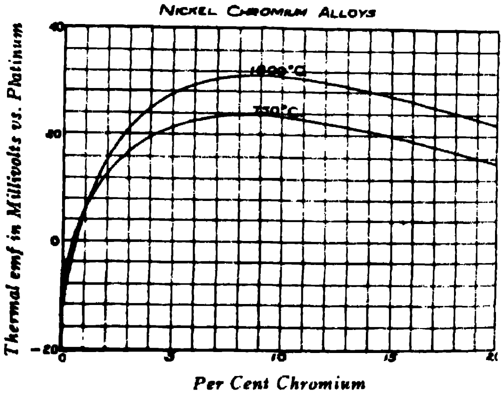

FIG. 1A.

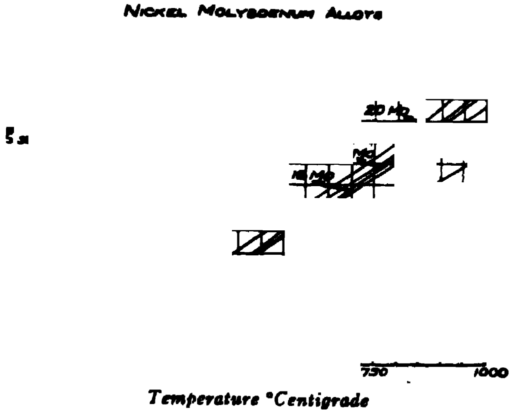

FIG. 2.

obtained with 20 per cent molybdenum is higher than the maximum obtained by chromium additions. In oxidizing atmospheres the molybdenum alloy is inferior to the chromium alloy. In reducing atmospheres it is superior as a thermocouple element (Fig. 2).

Table 3. Nickel-Chromium-Molybdenum Alloys.[3]

Composition			Emf at 1000 °C (mv)
Ni	Mo	Cr	
84.6	5	9.4	29.7
80.0	10	8.9	29.4
75.5	15	8.4	27.6
75.2	18.8	5.0	29.2
71.2	17.8	10.0	24.6
83.0	13.8	3.2	34.1
86.5	6.9	6.6	33.0

The manganese content of each of these alloys was 1 per cent. The last two alloys are superior in emf to alloys with comparable chromium content. The effect of chromium additions to nickel-molybdenum alloys of high molybdenum content results in lowering the emf (Fig. 3).

Nickel Chromium Molybdenum Alloys

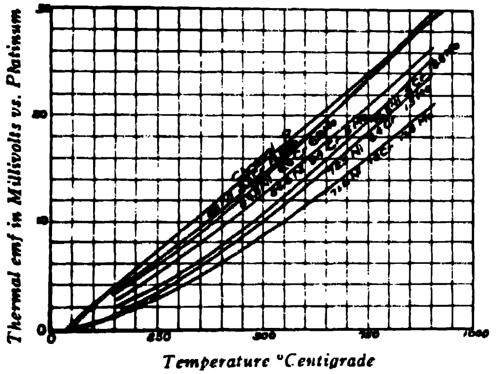

FIG. 3.

Table 4. Iron-Molybdenum Alloys.[4]

Composition			Emf at 1000 °C (mv)
Fe	Mo	Mn	
98	1	1	14.2
92	7	1	20.2

The magnitude of the emf in iron-molybdenum is of the same order as in nickel-molybdenum (Fig. 4).

Table 5. Nickel-Chromium Alloys with Aluminum and Silicon.[5]

Composition				Emf at 1000 °C (mv)
Ni	Cr	Al	Si	
80	20	.22		21.42
79.2	19.8	1.0		21.04
77.6	19.4	2.9		16.97
76.2	19.1	4.8		17.40
78.4	19.6		1.96	18.70
76.2	19.1		4.8	16.54

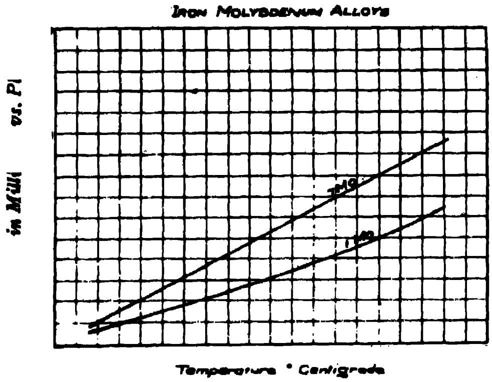

FIG. 4.

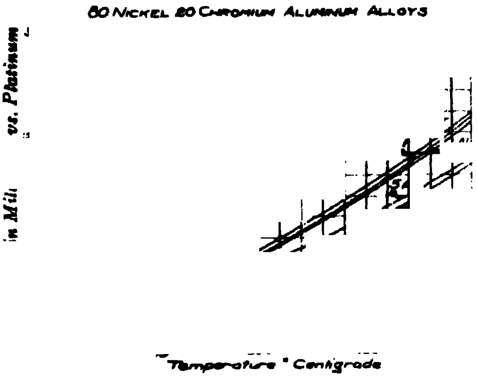

FIG. 5.

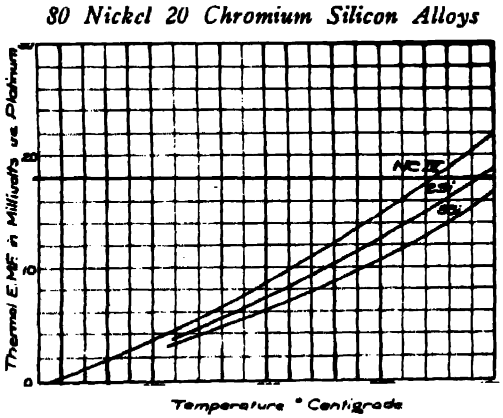

FIG. 5A.

Additions of aluminum or silicon can be made to nickel-chromium alloys to improve resistance to oxygen or sulfur at elevated temperatures. The addition results in lowering the emf of the alloy (Figs. 5 and 5A).

Nickel-Iron-Tungsten Alloys[6]

The previous tables and curves have indicated that chromium and molybdenum are desirable additions to nickel or iron or nickel and iron. The addition of tungsten produces alloys which are undesirable as thermocouple materials. The emf-temperature curves for additions of tungsten to 70 iron-30 nickel, to 50 iron-50 nickel, and to 30 iron-70 nickel in all cases show inversion points.

Cobalt-Chromium Alloys[7]

For purposes of comparison with nickel-chromium alloys, the emf for some cobalt-chromium alloys were determined. The alloys are much inferior to nickel-chromium as thermocouple material. The magnitude of the emf is small and the curves are non-linear.

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The Thermal Electromotive Force of Various Metals and Alloys

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Thermal emf values for a variety of metals and alloys have been published by various workers. Data presented herewith cover information on a large group of alloys made by the Driver-Harris Company, as well as several alloys from other sources. In addition, some data already published by the National Bureau of Standards on pure iron, pure copper, Advance, Chromel and Alumel versus platinum (see Table 1) are included for reference.

The purpose of this paper, then, is to present a conveniently assembled group of data on this subject, and to make available to all interested the results of measurements made in the Driver-Harris Laboratory.

Those elements which give a positive emf to platinum were checked against Standard Chromel, while those having a negative emf to platinum were checked against Standard Alumel. Both the Chromel and Alumel had been previously calibrated against platinum by the Bureau of Standards. The values against platinum were then computed.

The samples were tested in a vertical tube furnace, the temperature of which was measured by a Standard Chromel-Alumel thermocouple, and read on a type "K" potentiometer.

In each case the sample being tested was welded to the standard and the thermal emf was taken at 200 °F-intervals, with the cold junction at 68 °F.

Table 1. Typical Analyses.

Alloy	C	Mn	Si	Cr	Fe	Cu	Ni
1. Chromel P			Nickel-Chromium				
2. Nirex[b]	.05	1.02	.24	13.15	5.58		Bal.
3. 105 Alloy[b]		2.11	.11	3.85			Bal.
4. Nichrome V[b]	.03	1.00	.69	18.85	.33		Bal.
5. Nichrome[b]		2.02	.35	14.93	Bal.		62.11
6. Copper[a]							
7. 525 Alloy[b]		1.37	.14	16.02	Bal.		36.40
8. Iron[a]							
9. K A 2[b] (Type 304)	.11	.50	.74	21.26	Bal.		9.67
10. Nickel (+.17 Cr)[b]		.28	.03	.17			Bal.
11. D Nickel[c]		5.06	.06				Bal.
12. R - 63[b]		4.08	1.01				Bal.
13. Alumel			Nickel-Aluminum				
14. E Nickel[c]		1.91	.11				Bal.
15. R - 65[b]		1.14	.17				Bal.
16. A Nickel[c]		.02	.08				Bal.
17. No. 99 Alloy[b]	.02	.01	.01				Bal.
18. Advance[b]						55	Bal.

[a] Regular Thermocouple Iron and Copper (Bureau Stds. R. P. 1080).
[b] Driver-Harris Alloys.
[c] International Nickel Co. Alloys.

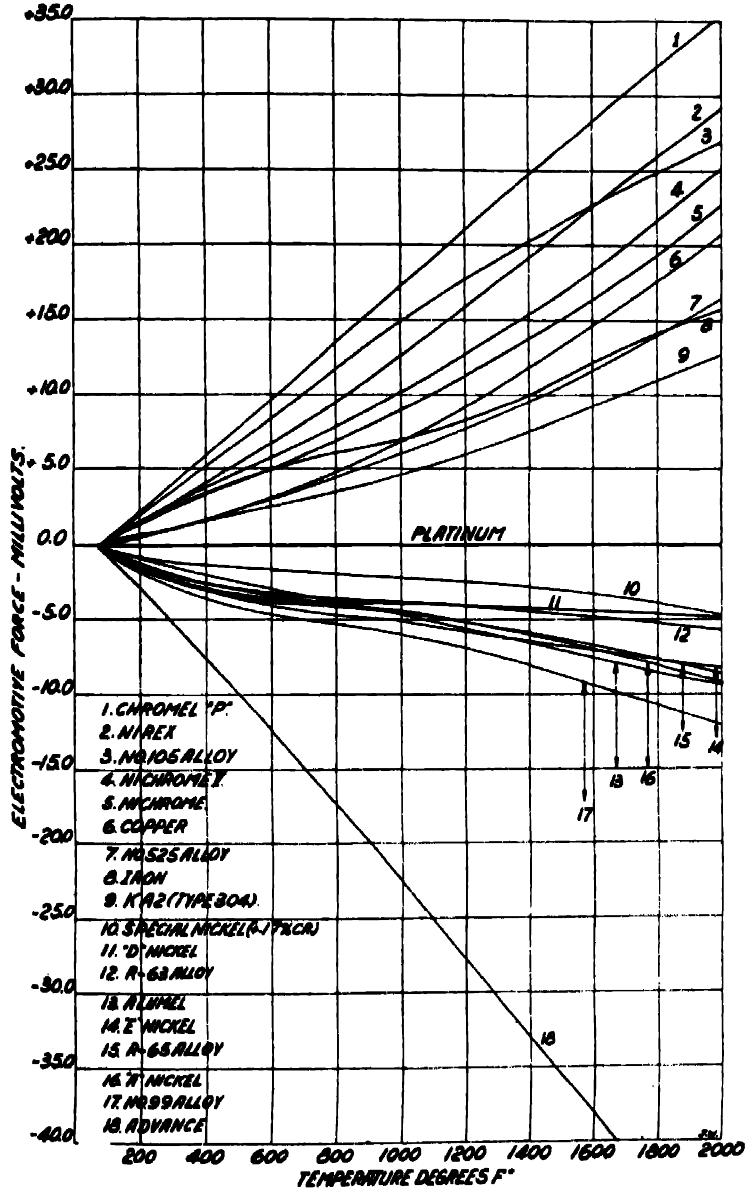

Fig. 1. Thermal emf of metals and alloys vs. platinum.

Fig. 1 shows the relationship of all the alloys under consideration to platinum, which is shown as the base line. Tables 2 and 3 show the data from which the curves have been plotted.

Table 2. Thermal Emf of Alloys Positive to Platinum.

(Cold Junction 68 °F)

Temp. (°F)	Nirex (2)	No. 105 Alloy (3)	Nichrome V (4)	Nichrome (5)	No. 525 Alloy (7)	KA 2 Type 304 (9)
200°	+ 1.91	+ 2.36	+ 1.81	+ 1.61	+ 1.14	+ 1.11
400	+ 4.21	+ 5.34	+ 3.81	+ 3.41	+ 1.91	+ 1.71
600	+ 6.88	+ 8.55	+ 5.95	+ 5.25	+ 3.15	+ 2.67
800	+ 9.72	+11.77	+ 7.97	+ 7.07	+ 4.49	+ 3.57
1000	+12.65	+14.80	+10.30	+ 9.00	+ 6.10	+ 4.65
1200	+15.81	+17.86	+12.76	+11.25	+ 7.86	+ 5.86
1400	+19.13	+20.33	+15.48	+13.73	+ 9.63	+ 7.33
1600	+22.60	+22.80	+18.40	+16.50	+11.80	+ 9.00
1800	+26.18	+25.13	+21.58	+19.43	+14.18	+10.98

(Cold Junction 32 °F)

Temp. (°F)	Chromel P vs. Platinum[a]	Copper vs. Platinum[b]	Iron vs. Platinum[b]
200	+ 2.61	+ .70	+ 1.77
400	+ 6.11	+ 1.88	+ 3.60
600	+ 9.85	+ 3.37	+ 5.03
800	+13.67	+ 5.12	+ 6.12
1000	+17.50	+ 7.12	+ 7.15
1200	+21.26	+ 9.37	+ 8.40
1400	+24.93	+11.88	+10.13
1600	+28.50	+14.65	+12.25
1800	+31.98	+17.69	+14.03
2000	+35.36		
2200	+38.64		

[a] National Bureau of Standards Research Paper, RP 767.

[b] National Bureau of Standards Research Paper, RP 1080.

Conclusion

It should be noted that all the alloys containing nickel plus appreciable proportions of chromium are positive to platinum, while those composed mainly of nickel with additions of manganese and silicon are negative to platinum. A comparison of curves No. 10 and No. 17 shows the positive effect on nickel of even a small proportion of chromium. On the other hand, a comparison of curves No. 8 and No. 9 (iron and KA2, type 304) shows the comparatively small effect of chromium and nickel on iron.

In applying the foregoing data for making thermocouples, considerable care should be used in selecting the proper alloys, because a thermocouple should possess these properties:

(1) Ability to resist corrosion and oxidation.
(2) Relatively large emfs.
(3) A linear emf curve.
(4) Uniformity of material for reproducibility.

Table 3. Thermal Emf of Alloys Negative to Platinum.

(Cold Junction 68 °F)

Temp. (°F)	Spec. Nickel + .17 Cr (10)	D Nickel (11)	No. 63 Alloy (12)
200	-0.84	-1.56	-1.51
400	-1.30	-2.90	-2.60
600	-1.55	-3.70	-3.08
800	-1.85	-3.85	-3.30
1000	-2.15	-3.95	-3.95
1200	-2.42	-4.07	-4.07
1400	-2.87	-4.27	-4.42
1600	-3.30	-4.45	-4.90
1800	-3.84	-4.64	-5.14

Temp. (°F)	E Nickel (14)	R-65 Alloy (15)	A Nickel (16)	No. 99 Alloy (17)
200	-1.27	-1.22	-0.99	-1.71
400	-3.03	-2.70	-2.25	-3.40
600	-4.185	-3.83	-3.395	-4.60
800	-5.57	-4.075	-3.915	-5.45
1000	-5.01	-4.76	-4.435	-6.05
1200	-5.52	-5.385	-5.16	-6.92
1400	-6.125	-6.11	-6.045	-8.09
1600	-6.80	-6.91	-7.06	-9.40
1800	-7.505	-7.775	-8.19	-10.84
2000	-8.25	-8.69	-9.43	
2200	-9.06	-9.68	-10.77	

(Cold Junction 32 °F)

Temp. (°F)	Alumel vs. Platinum[a]	Advance vs. Platinum[b]
200	- 1.21	- 3.26
400	- 2.20	- 7.64
600	- 3.00	-12.40
800	- 3.85	-17.41
1000	- 4.75	-22.55
1200	- 5.72	-27.77
1400	- 6.72	-32.99
1600	- 7.70	-38.14
1800	- 8.64	-43.13
2000	- 9.53	
2200	-10.37	

[a] National Bureau of Standards, Research Paper RP 767.

[b] National Bureau of Standards, Research Paper RP 1080.

Most of the alloys here considered would satisfy requirements (1) and (2) under many conditions. Few of them would satisfy requirement (3), since most do not have truly linear temperature-emf relationships.

Regarding (4) the emf values for the non-standard alloys listed may be subject to adjustment before a curve is obtained which could be reproduced commercially.

Alloys of Iron and Nickel in Resistance Thermometry

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Many surveys of the physical properties of alloys in the iron-nickel system have appeared in published literature.[1] The results show natural discrepancies due to variation in impurities in the alloys used in the different investigations. In the main, however, the observations indicate that alloys containing 70 per cent of nickel and 30 per cent of iron have higher temperature coefficients of electrical resistivity than any other alloy in the system. Since these alloys have, in addition, high specific resistance, high temperatures of magnetic transformation and excellent resistance to oxidation at elevated temperatures, they offer great possibilities for use in resistance thermometers and in other temperature-controlling devices which operate on changes in electric resistance.

Data on electric resistance and temperature coefficient of electric resistance for three commercial alloys of this type are given in this paper. Observations have been made on three alloys varying somewhat in manganese and silicon content.

Melt A: Mn 00%; Si .05%

The temperature coefficient was measured on a sample after aging for 48 hours at 120 °C.

Temperature (°C)	Relative Resistance	Mean Temperature Coefficient 0° to *T*
0	1.000	
10	1.044	.00444
25	1.112	.00448
50	1.229	.00459
75	1.352	.00469
100	1.483	.00483

Melt B: Mn .07%; Si .19%

Samples were aged for 18 hours at 140 °C. The mean value of the temperature coefficient taken on eight samples over the range 0 to 100 °C was .00443 per °C (maximum .00443, minimum .00439). No intermediate readings were taken.

Melt C: Mn .48%; Si .22%

Observations on this alloy were made in hydrogen over a temperature range of 28-1000 °C.

It will be noted from observations of these three alloys that the temperature coefficient is higher in alloys of the higher purity. From observations on Melt C it is also evident that the temperature coefficient rises with increasing temperature up to 600 °C, the temperature of magnetic transformation.

Temperature (°C)	Relative Resistance	Mean Temperature Coefficient 28 ° to *T*
28	1.000	.....
100	1.319	.00443
200	1.841	.00488
300	2.306	.00480
400	2.887	.00507
500	3.503	.00530
550	3.889	.00552
600	4.282	.00574
650	4.396	.00546
700	4.456	.00514
800	4.522	.00456
900	4.593	.00412
1000	4.683	.00379

Specific Resistance

The specific resistances of the alloys are directly related to their manganese and silicon content. The alloy with the lowest percentage of impurity (Melt A) has a specific resistance of 121 ohms per cir. mil-ft, while the alloy with the highest percentage of impurity has a specific resistance of 132 ohms per cir. mil-ft. These values are approximately three times that of pure nickel, which has previously been used in resistance thermometry.

Resistance to Oxidation

While it is not possible to give exact data on oxidation resistance, it can be indicated that this type of alloy has been used in electric heating elements at temperatures over 600 °C and has given satisfaction.

Conclusions

It is felt that the unique combination of high electrical resistance and high temperature coefficient of electrical resistance over a wide range in temperature may be useful to designers of modern instruments for thermometry.

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The Stability of Base-metal Thermocouples in Air from 800 to 2200 °F.

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National Bureau of Standards, Washington, D. C.

I. Introduction

With the widespread use of base-metal thermocouples for temperature measurement and control in industrial processes there are numerous instances where high accuracy is of vital importance. Some processes require that a given temperature be maintained within narrow limits for an extended period of time if efficiency in operation and uniformity in production are to be maintained. In order to meet these requirements a more complete knowledge of the thermoelectric stability of base-metal thermocouple materials is necessary.

Practically all base-metal thermocouple wire produced in this country is annealed or given a stabilizing heat treatment by the manufacturer. For most purposes this treatment renders the product sufficiently stable so that further changes which may occur while the thermocouple is in service may be neglected. However, when high accuracy is required throughout the useful life of the thermocouple, these changes must be taken into account. In many industrial processes, thermocouples, when placed in service, are left undisturbed until there is evidence of either mechanical failure or serious error in the temperatures indicated. However, long before this occurs, the thermocouple may have changed to such an extent as to make it unreliable for accurate temperature measurement. The changes in the thermoelectric characteristics of thermocouple materials due to ordinary service conditions are usually gradual and cumulative. They depend upon such factors as the temperatures encountered, the length of time in service, and the atmosphere surrounding the thermocouple. The various types of thermocouple materials are affected in various ways and to various degrees.

When the reference-junction temperature is maintained constant, the emf developed by a homogeneous thermocouple depends only on the temperature of the measuring junction. The emf developed by an inhomogeneous thermocouple depends not only on the temperature of the measuring junction but also on the temperature distribution throughout the inhomogeneous portions of the wires. All base-metal thermocouples become inhomogeneous with use at high temperatures. However, if all the inhomogeneous portions of the thermocouple wires are in a region of uniform temperature, the inhomogeneous portions have no effect upon the indications of the thermocouple. Therefore, an increase in the depth of immersion of a used couple has the effect of bringing previously unheated portions of the wires into the region of temperature gradient, and thus the indications of the thermocouple will correspond to the original emf-temperature relation, provided the increase in immersion is sufficient to bring all the previously heated part of the wires within the zone of uniform temperature. If the immersion is decreased, the more inhomogeneous portions of the wires will be brought into the region of temperature gradient, thus giving rise to a change in the indicated emf. Furthermore, a change in the temperature distribution along inhomogeneous portions of the wire nearly always occurs when a couple is removed from one installation and

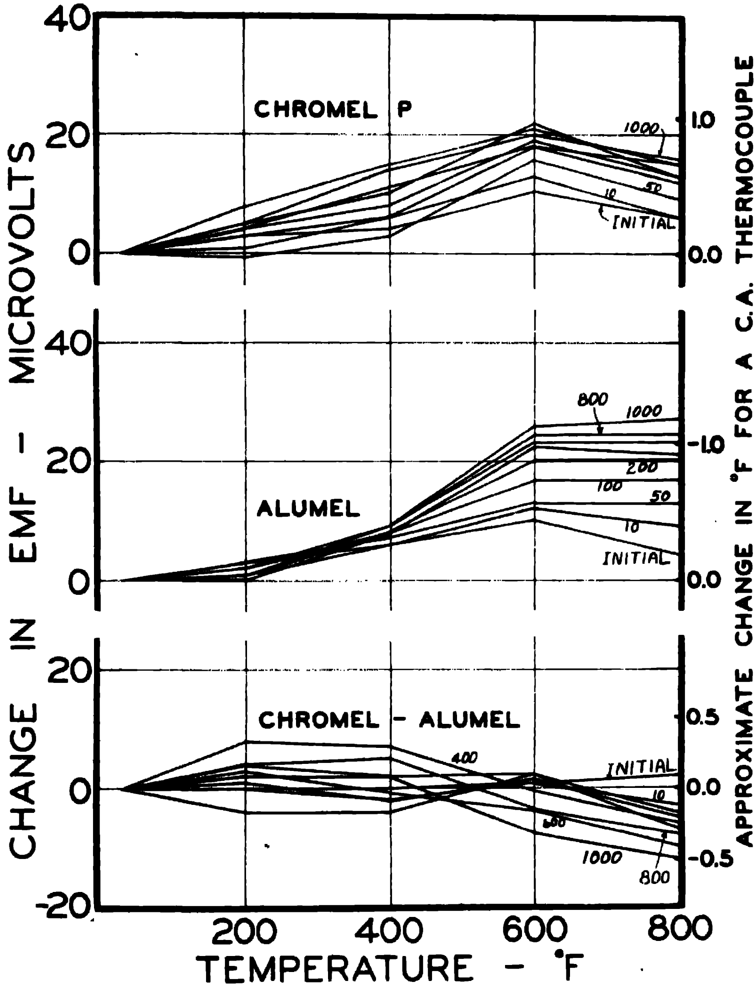

FIG. 1. Changes in No. 18-gage Chromel P and Alumel due to heating in air at 800 °F for the total times indicated on the graphs.

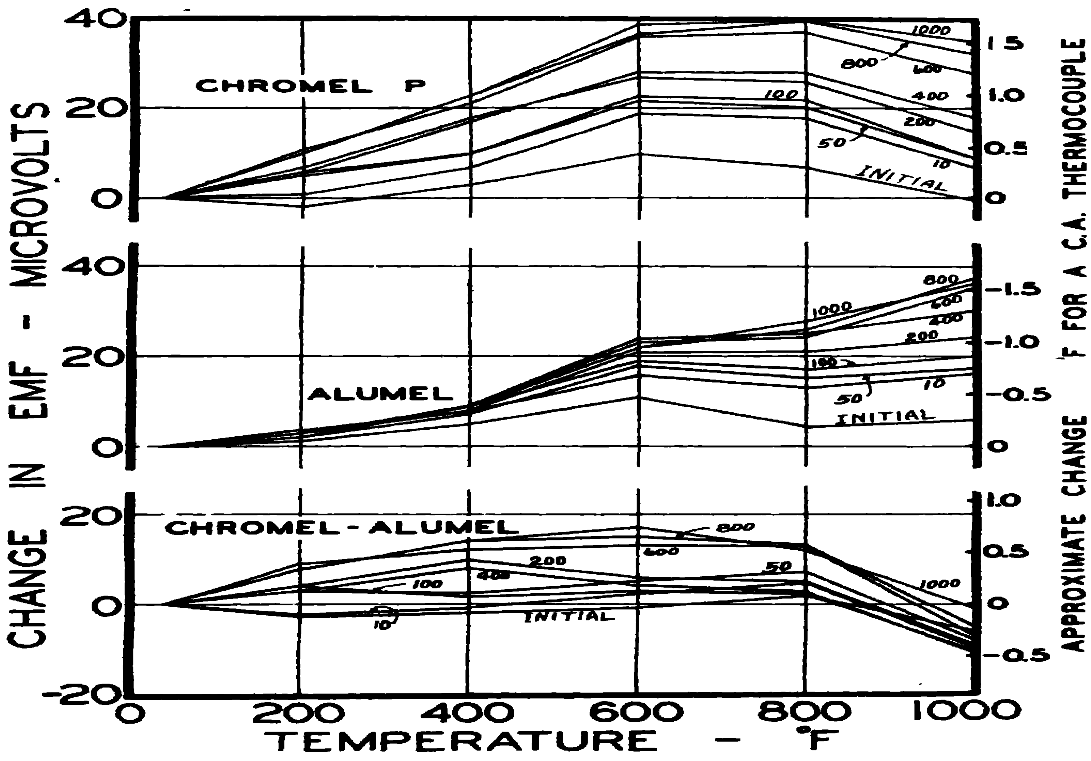

FIG. 2. Changes in No. 18-gage Chromel P and Alumel due to heating in air at 1000 °F for the total times indicated on the graphs.

placed in another, even though the measured immersion and the temperature of the measuring junction are the same in both cases. Thus the indicated emf is changed.

Although it is recognized that there are differences in composition and thermoelectric properties between various lots of thermocouple materials of the same general type, it is believed that the changes in the thermoelectric properties of a few selected lots of material will give a general idea of the changes which would occur in other lots of the same general type, providing that all lots have received the same initial heat treatment.

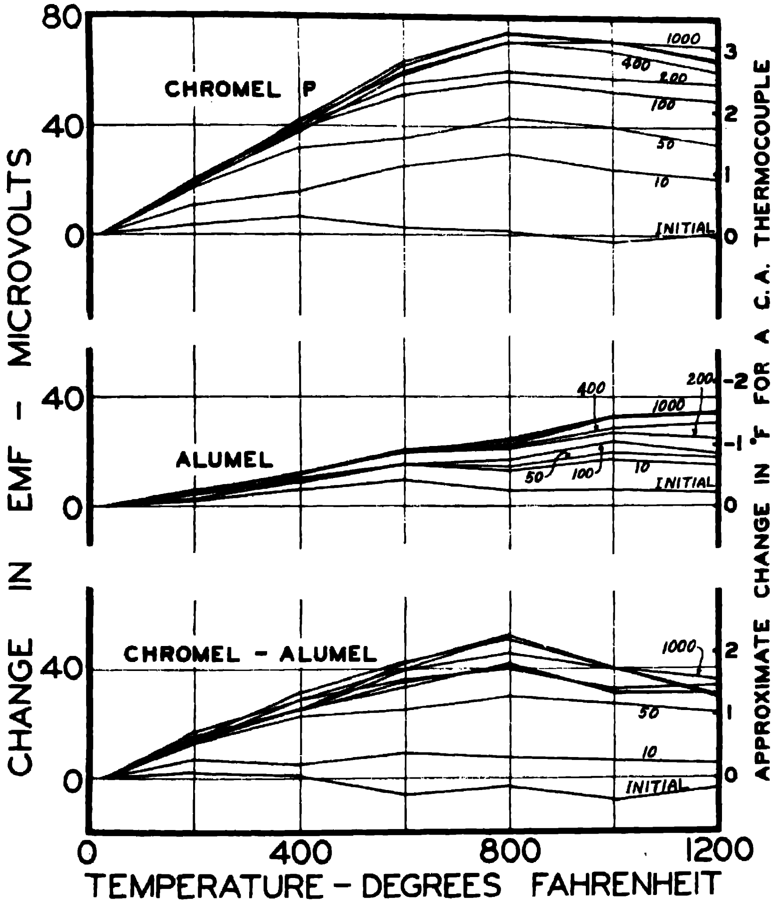

FIG. 3. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1200 °F for the total times indicated on the graphs.

II. Materials Investigated

The thermocouple materials studied were Chromel P, Alumel, iron, and constantan. Chromel P and Alumel wire of No. 18 gage, and iron and constantan of No. 14 gage were used for the tests at 800 and 1000 °F. For the test at 1200 °F and above, No. 8-gage wires were used. To determine the relation of wire size to the thermoelectric stability, additional tests were made on No. 18- and No.

22-gage Chromel P and Alumel at 1200 and 1600 °F, and on No. 18-gage iron and constantan at 1200 and 1400 °F.

Samples of the various materials were secured from several sources. Each of the materials used in the investigation had the temperature-emf relation characteristic of the large percentage of the material of its particular type now being manufactured. All the wires had been heat-treated by the manufacturers in the manner considered standard for the particular type of wire.

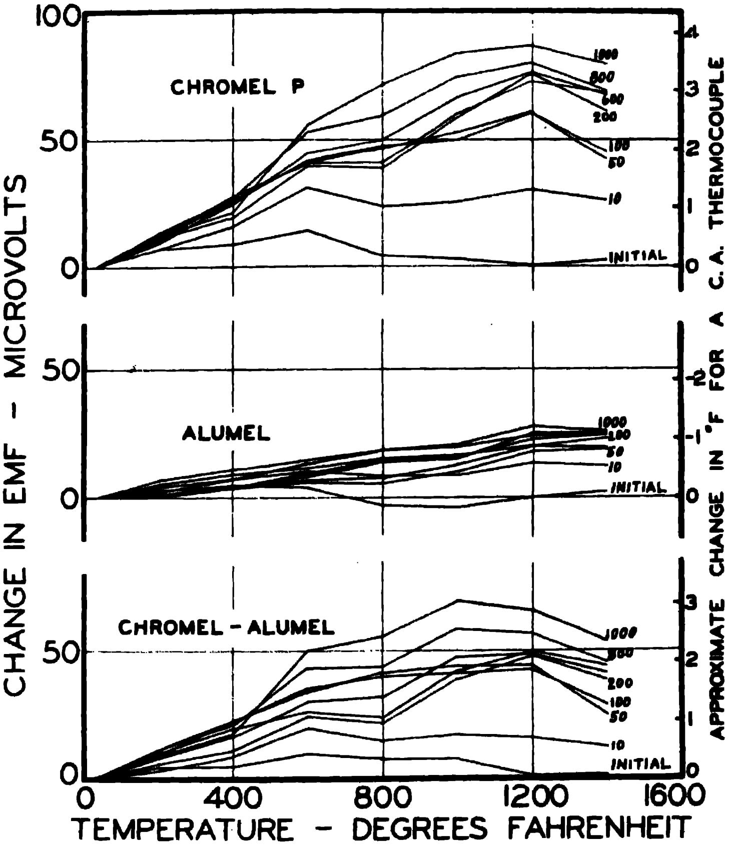

FIG. 4. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1400 °F for the total times indicated on the graphs.

III. Test Methods

Since Chromel P is generally used in combination with Alumel, and iron with constantan, the materials were paired in this manner. In addition to determining the temperature-emf relation for each pair, the thermal emf of the individual elements of each pair against the platinum standard,[1] Pt 27, was determined. In this way the thermoelectric changes of each thermocouple material were determined independently. The difference of the thermal emfs of the individual elements of a thermocouple against a third material is equal to the emf of the thermocouple. As all three were measured in this work, any two served as a check upon the third.

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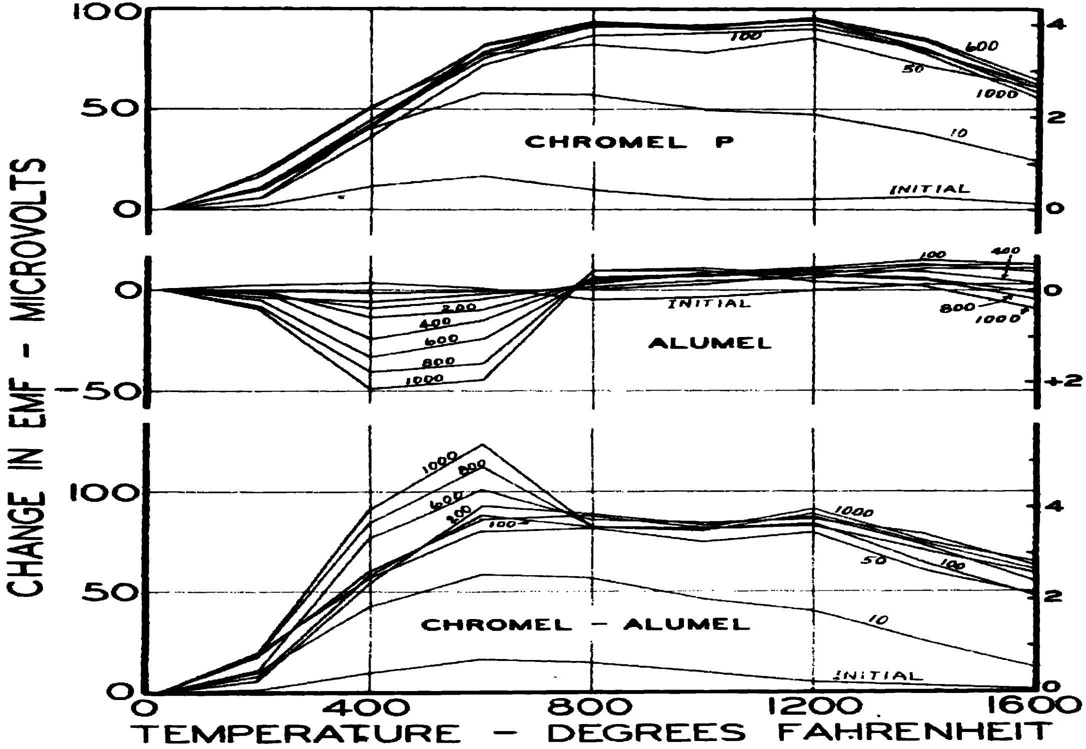

FIG. 5. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1600 °F for the total times indicated on the graphs.

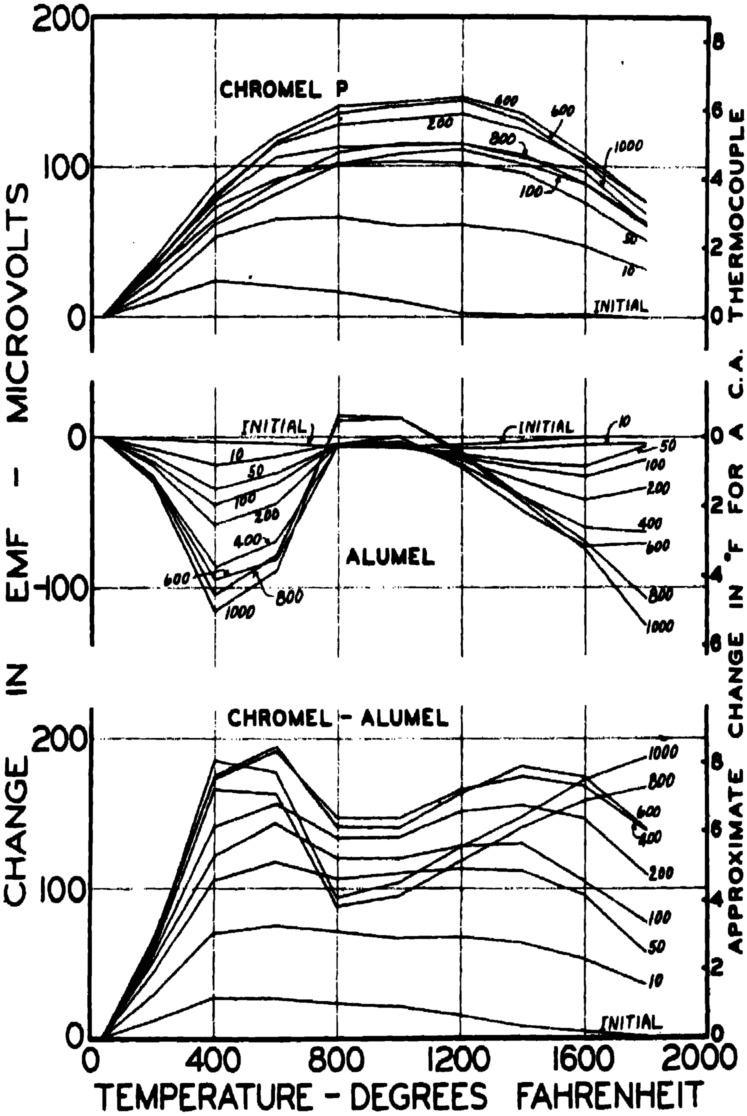

Fig. 6. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 1800 °F for the total times indicated on the graphs.

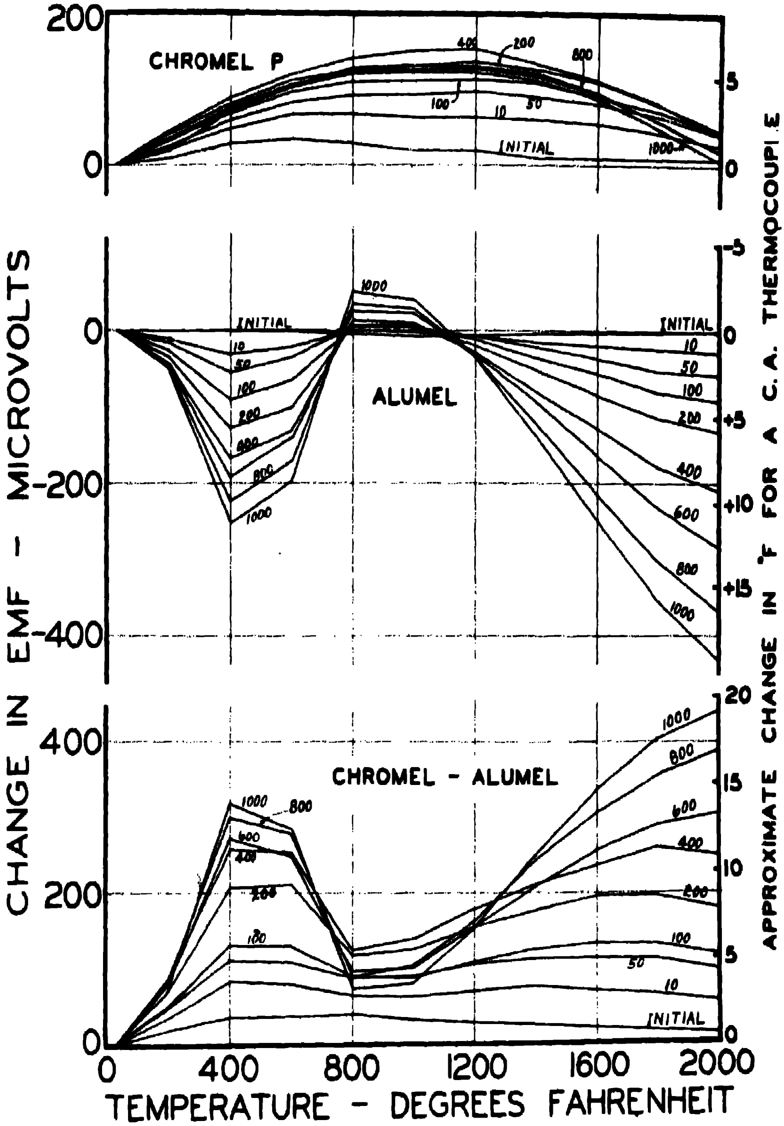

Fig. 7. Changes in No. 8-gage Chromel P and Alumel due to heating in air at 2000 °F for the total times indicated on the graphs.

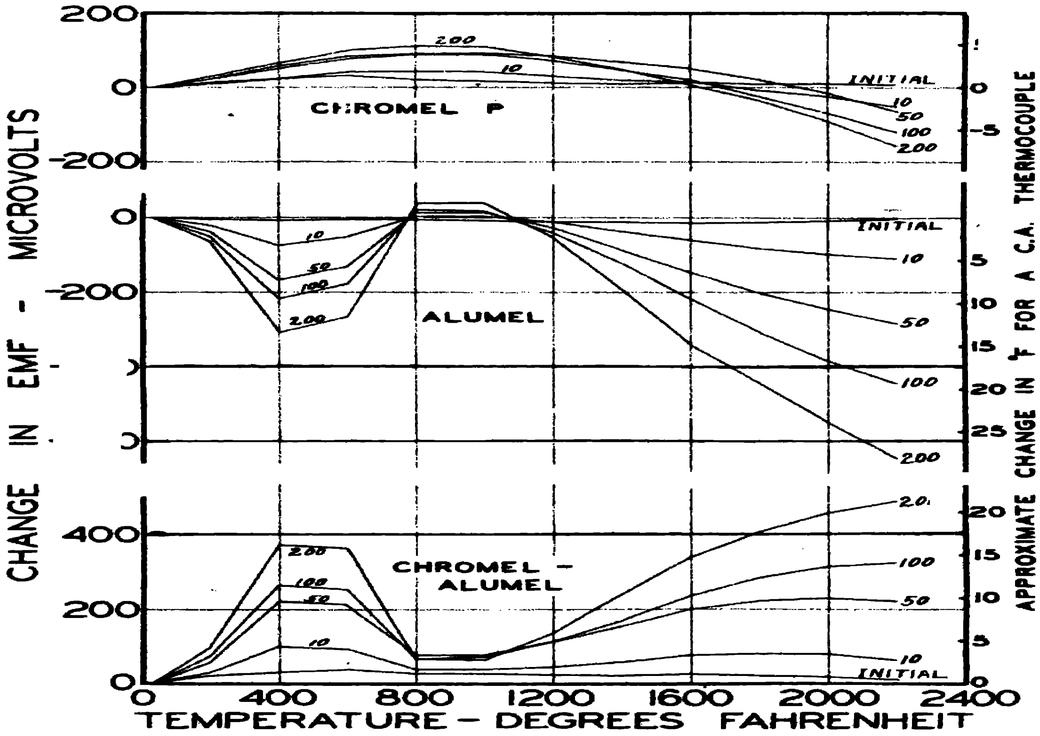

FIG Changes in No. 8-gage Chromel P and Alumel due to heating in air at 2200 °F for the total times indicated on the graphs.

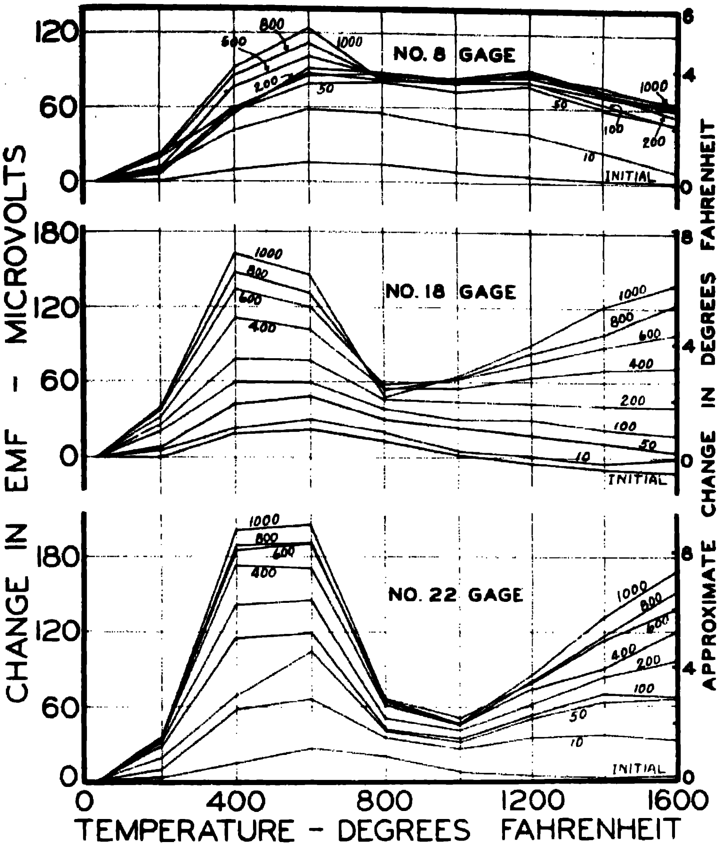

FIG. 9. Changes in No. 8, No. 18, and No. 22-gage Chromel-Alumel thermocouples due to heating in air at 1600 °F for the total times indicated on the graphs.

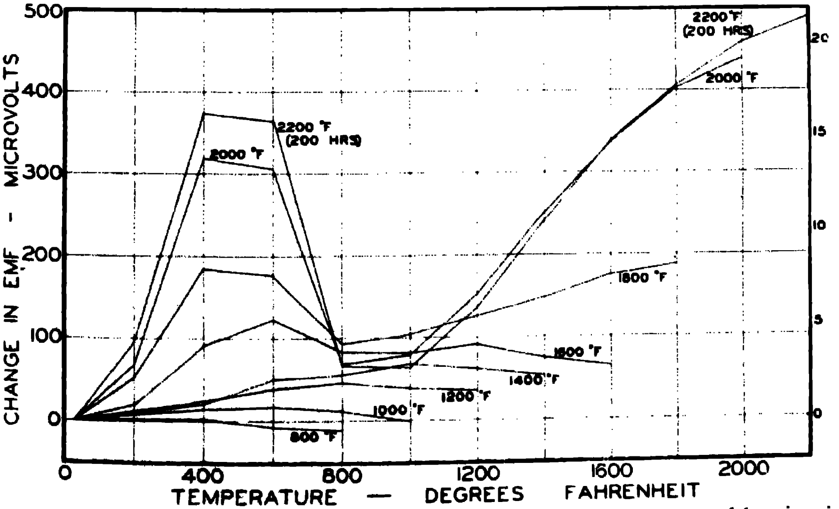

FIG. 10. Changes in Chromel-Alumel thermocouples due to 1000 hours of heating in air at temperatures indicated on the graphs.

The temperatures were measured with a standard platinum to platinum-10 per cent rhodium thermocouple calibrated in accordance with the specifications for the International Temperature Scale.[2] The platinum working standard used was checked periodically against Pt 27.

The pair or pairs of wire under test were insulated by 2-hole porcelain insulators. The platinum reference wire was protected by a glazed porcelain tube and was sealed through the end of the protection tube with a "Pyrex" glass, leaving about 1 cm of the end of the wire protruding beyond the seal. The platinum-rhodium thermocouple, insulated with a 2-hole porcelain tube inside a glazed porcelain protection tube, was likewise sealed through the end of its protection tube with a "Pyrex" glass, leaving the welded junction protruding about 1 cm beyond the seal. The ends of the base metal wires, the platinum reference wire and the standard thermocouple were then welded together to form a single composite junction.

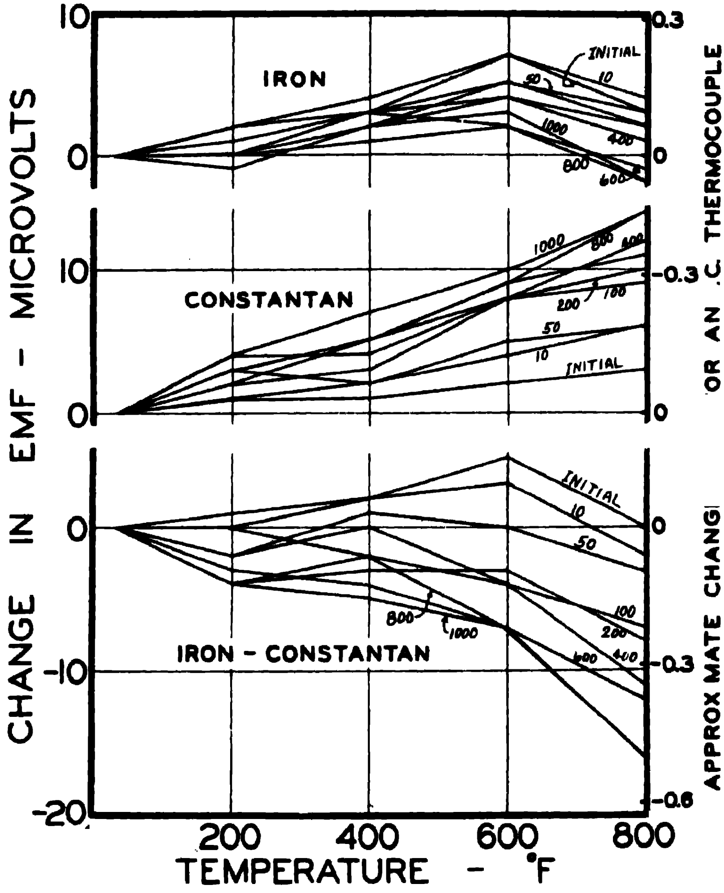

FIG. 11. Changes in No. 14-gage iron and constantan due to heating in air at 800 °F for the total times indicated on the graphs.

The furnace used in this work was of the resistance type wound with platinum rhodium wire. The furnace tube of Alundum was 60 cm long and 3 cm inside diameter. The wires under test, together with the platinum reference wire and the platinum-rhodium thermocouple, were placed in the furnace with the composite junction at about the midpoint. The wires were then securely clamped with respect to the furnace. Although the ends of the furnace tube were closed with asbestos wool to promote temperature uniformity, no attempt was made to exclude air from

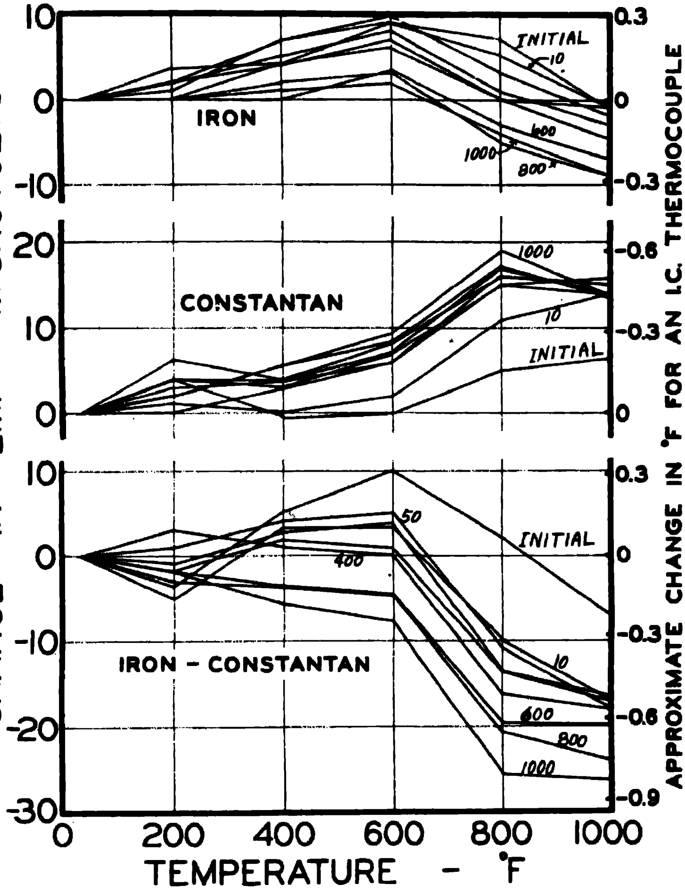

Fig. 12. Changes in No. 14-gage iron and constantan due to heating in air at 1000 °F for the total times indicated on the graphs.

the heated chamber, so that the atmosphere prevailing within the tube was oxidizing. The reference junctions were maintained at 32 °F during all the measurements. The temperature of the furnace was maintained practically constant during any observation at a given point by means of a hand-operated voltage regulator in the power circuit.

To obtain data on the effect of long-time exposure to high temperatures upon the thermoelectric properties of the materials the following procedure was adopted. The initial measurements were made on the sample as received from the manufacturer. Measurements of the thermal emfs of the various combinations were made at intervals of 200 °F, up to and including in each case the temperature at which the effect of heating was to be determined. The furnace was then allowed to cool to room temperature and the measurements repeated. The differences between the two sets of measurements were ascribed to the initial heating and will be referred to as the "initial changes." Similar measurements were then made after the materials had been held at the test temperature for total elapsed times of 10, 50, 100, 200, 400, 600, 800, and 1000 hours, or as long as the materials remained serviceable. The test temperatures included every temperature from 800 °F to and including 2000 °F in steps of 200 °F. Chromel P and Alumel were also tested at 2200 °F. A fresh sample was used for the test at each temperature. During heating periods the temperature of the furnace was maintained constant within ± 5 °F by means of an automatic temperature controller.

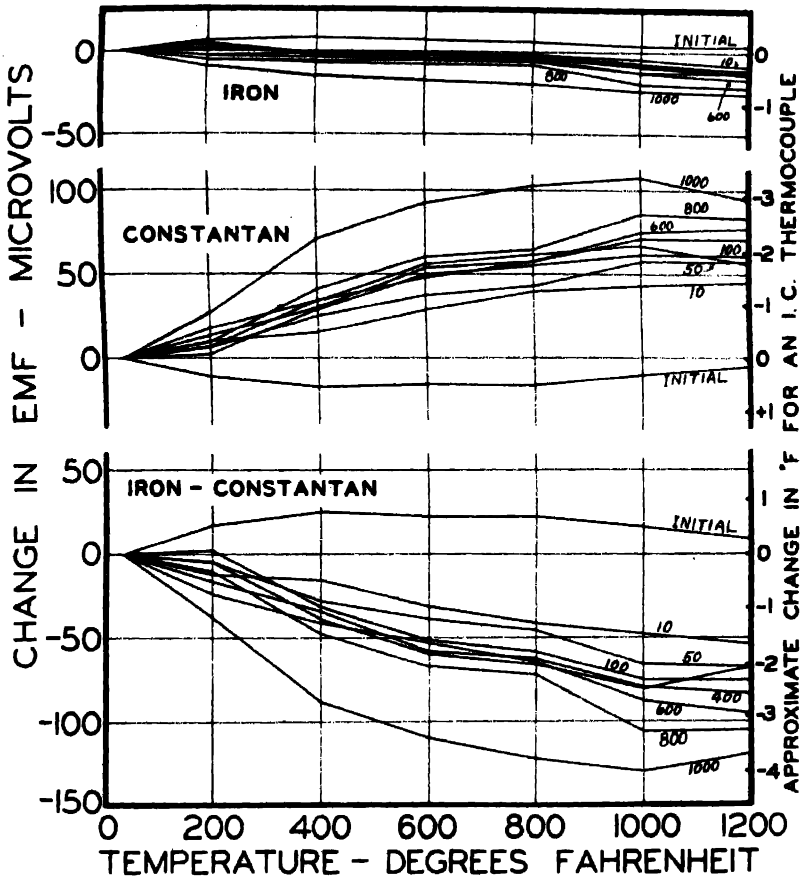

FIG. 13. Changes in No. 8-gage iron and constantan due to heating in air at 1200 °F for the total times indicated on the graphs.

The procedure followed in studying the effect of decreasing the depth of immersion was as follows. The materials were heated in the electric furnace for a period of 20 hours at a constant temperature. Following this heat treatment the thermal

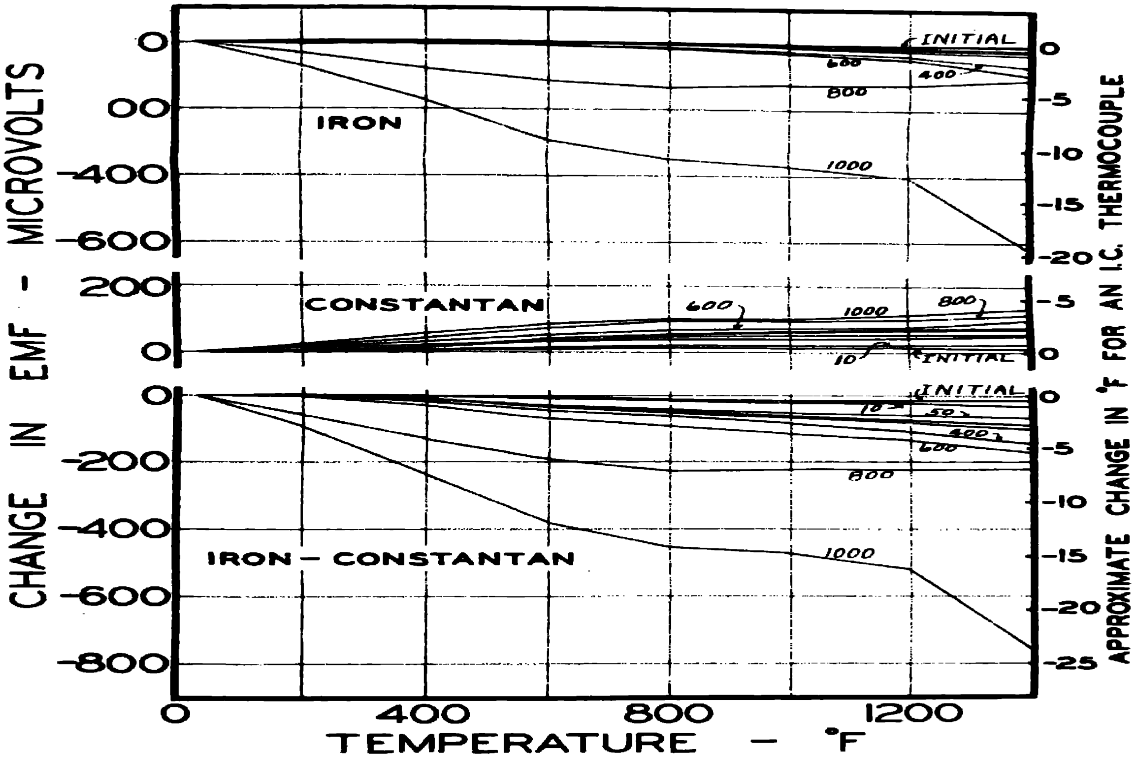

Fig. 14. Changes in No. 8-gage iron and constantan due to heating in air at 1400 °F for the total times indicated on the graphs.

emf of the samples was determined, the position of the samples being maintained the same as that during the 20-hour heating period. The furnace was then allowed to cool to room temperature, the immersion was decreased 3 inches, and the thermal emfs were determined in this new position. The difference between the observations for a given sample is due only to the change in immersion, since no heating took place between the two sets of measurements. This type of test was carried out on No. 8-gage iron and constantan at temperatures from 600 to 1800 °F in 200 °F steps and on No. 8-gage Chromel P and Alumel from 600 to 2200 °F.

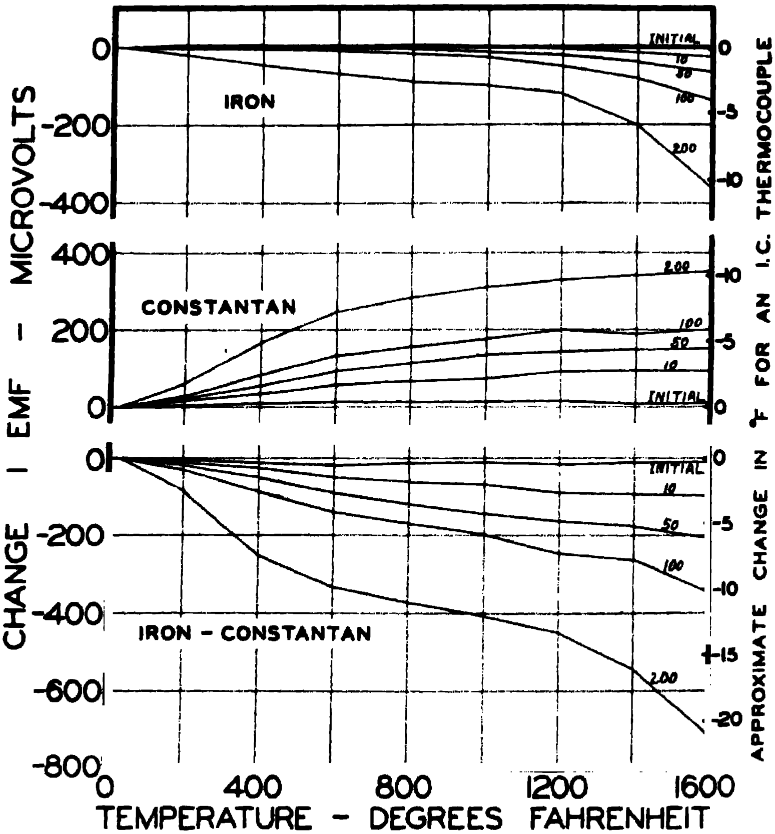

FIG. 15. Changes in No. 8-gage iron and constantan due to heating in air at 1600 °F for the total times indicated on the graphs.

IV. Results

A. Temperature Exposure Tests

1. Chromel P and Alumel. Figs. 1 and 2 show the results obtained on No. 18-gage Chromel P and Alumel heated at 800 and 1000 °F, respectively. The changes in the completed Chromel-Alumel thermocouples are also shown. The changes in the individual elements are in the same direction, so that each becomes thermoelectrically positive to the material in its original condition. The convention followed in regard to sign is as follows. If in a simple thermoelectric circuit the current flows from metal A to metal B at the colder junction, A is thermoelectrically positive to B. On the basis of this convention Chromel P is positive to Alumel. Therefore a positive change in Chromel P will increase the emf of a Chromel-Alumel thermocouple, whereas a positive change in Alumel will decrease the emf of the thermocouple. The changes observed in the tests at 800 and 1000 °F are small, in all cases less than the equivalent of 1 °F for a Chromel-Alumel thermocouple.

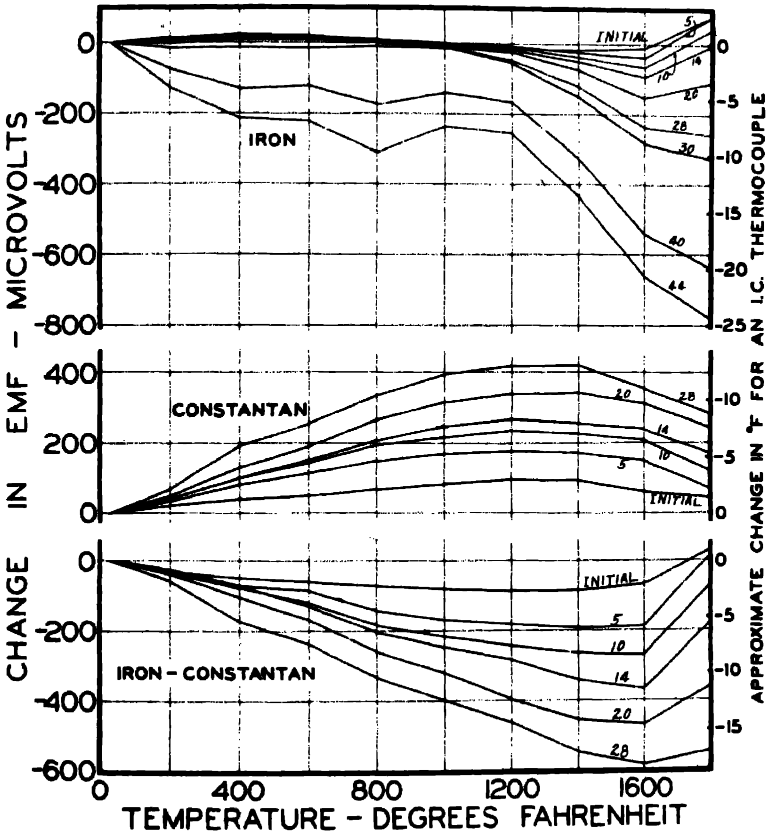

FIG. 16. Changes in No. 8-gage iron and constantan due to heating in air at 1800 °F for the total times indicated on the graphs.

Figs. 3 to 8 inclusive show the results obtained with No. 8-gage Chromel P and Alumel at temperatures from 1200 to 2200 °F inclusive. The changes in the emf of Chromel P are in the positive direction throughout all tests with the exception of the test at 2200 °F where a negative change was observed at temperatures above 1600 °F. The magnitude of the changes is in nearly all cases in the order of the duration of the heating periods, the maximum change occurring at about 1200 °F. The changes in the Alumel are in the positive direction throughout the tests at 1200 and 1400 °F. In the tests at 1600 °F and above, the changes in the emf of the Alumel between about 800 and 1100 °F are extremely small. Above 1100 °F the changes are negative and of appreciable magnitude. This is most clearly shown in Fig. 7. The materials used in the test at 2200 °F failed after about 300 hours of heating.

Tests of No. 8-, No. 18-, and No. 22-gage Chromel-Alumel thermocouples heated at 1200 °F for a total of 1000 hours indicated that the changes in the thermocouples of the various sizes were nearly the same and in all cases less than the equivalent of 2.5 °F. Fig. 9 shows the effects on the same sizes of Chromel-Alumel thermocouples when heated at 1600 °F. The change in calibration at 400 °F is largest in the smallest size, but the reverse is true for the change at 1000 °F.

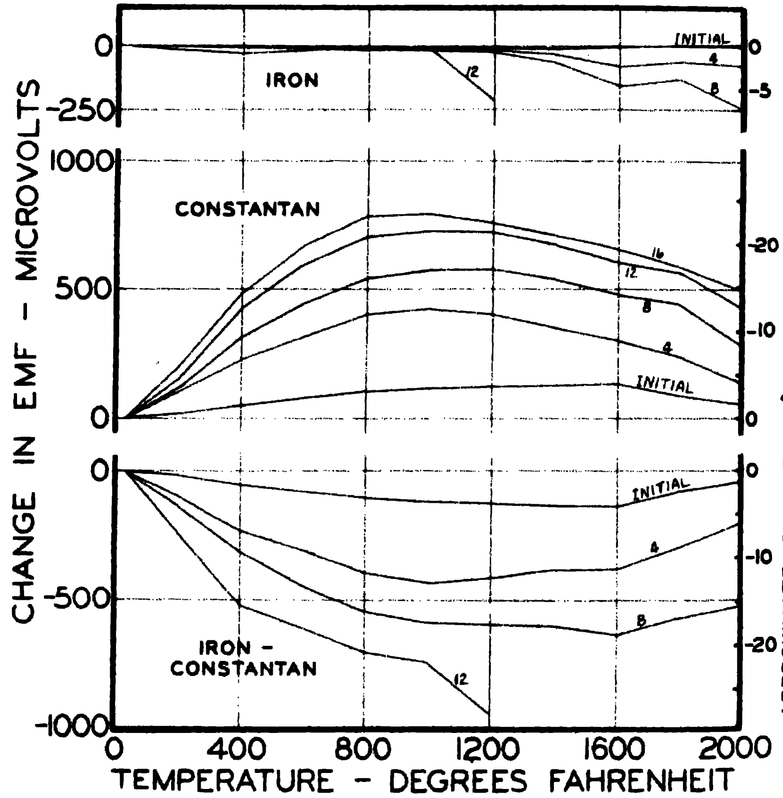

FIG. 17. Changes in No. 8-gage iron and constantan due to heating in air at 2000 °F for the total times indicated on the graphs.

The changes in the emf of the Chromel-Alumel thermocouples produced by the total heating time in each of the tests are shown in Fig. 10 (reproduced from Figs. 1 to 8, inclusive). In the test at 2200 °F the change after only 200 hours is shown, this being the elapsed time when the last measurements preceding failure were made. The peculiar change in the Alumel previously mentioned is reflected in change of the thermocouples.

2. Iron and Constantan. Figs. 11 and 12 show the results obtained on No. 14-gage iron and constantan tested at 800 and 1000 °F, respectively. The changes in all cases are small, being less than the equivalent of 1 °F.

The results on No. 8-gage iron and constantan tested at 1200 to 2000 °F inclusive are shown in Figs. 13 to 17. The time intervals between calibrations were shortened for the tests at 1800 and 2000 °F since at these temperatures the materials change at a rapid rate. The tests were continued until the materials failed.

The relative thermoelectric stability of No. 8- and No. 18-gage iron-constantan thermocouples heated at 1400 °F is shown in Fig. 18. As might be expected, the emf changes in the smaller wire proceed more rapidly. The No. 18-gage thermocouple failed after about 400 hours of heating, whereas the No. 8-gage remained serviceable throughout the 1000 hours of the test. However, the measurements made on the thermocouple at the end of the 1000-hour period indicated that failure was near. A test on these same sizes at 1200 °F showed no appreciable difference in their thermoelectric stability at this test temperature, the maximum change after 1000 hours of heating being about the equivalent of 4 °F.

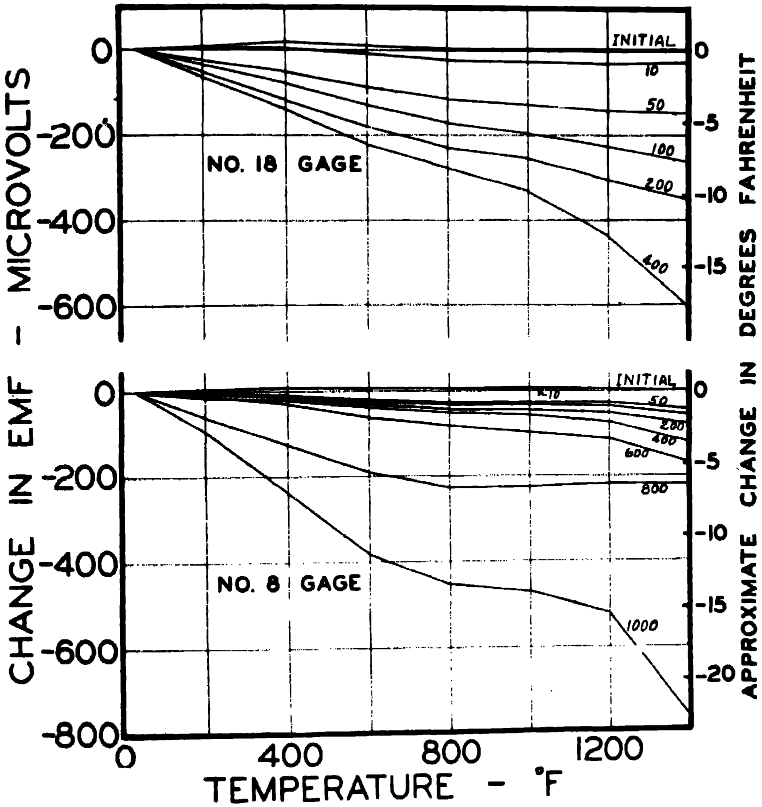

Fig. 18. Changes in No. 8 and No. 18-gage iron-constantan thermocouples due to heating in air at 1400 °F for the total times indicated on the graphs.

The change in the emf of constantan was gradual and cumulative throughout each test. In the case of iron, the change in emf was relatively small until failure of the wire was approached. When this stage was reached, the change was rapid and relatively large. This was true for all tests in which iron was heated until failure. The life of the iron element was found to be approximately the same as that of the constantan.

B. Immersion Tests

Table 1 gives the observed changes in the thermal emf of No. 8-gage iron and constantan produced by a 3-inch decrease in immersion following the 20-hour heating period. The changes in both of the elements are gradual and regular throughout, the magnitude of the emf changes in constantan being everywhere considerably greater than in the case of iron. Fig. 19 shows the change in the emf of the iron-constantan thermocouple under the various conditions of heating (test at 1800 °F not shown in graph). A greatly increased, though regular, change is clearly shown for the test at 1600 °F. At 1800 °F the change is about 4 times as great as that observed at 1600 °F.

Table 1. Changes (in microvolts) at Various Temperatures Caused by Decreasing the Depth of Immersion Three Inches after Heating in Air at the Temperatures Indicated for 20 Hours.

Calibration Temp. (°F)	Heating Temperature (°F)						
	600	800	1000	1200	1400	1600	1800
				Iron			
200	1	5	3	1	−2	−1	−2
400	0	7	4	3	−2	−4	−9
600	1	8	3	4	−2	−7	−18
800		7	2	4	−3	−12	−29
1000			3	4	−6	−19	−43
1200				1	−9	−30	−58
1400					−13	−43	−72
1600						−57	−80
1800							
				Constantan			
200	4	10	13	14	14	25	83
400	7	18	20	30	28	62	224
600	9	27	26	43	41	93	374
800		35	37	52	53	127	504
1000			49	60	54	156	615
1200				65	65	182	735
1400					68	208	837
1600						223	935
1800							1078
				Iron-Constantan			
200	−3	−5	−10	−13	−16	−26	−85
400	−7	−11	−16	−27	−30	−66	−233
600	−8	−19	−23	−39	−43	−100	−392
800		−28	−35	−48	−56	−139	−533
1000			−46	−56	−60	−175	−658
1200				−64	−74	−212	−793
1400					−81	−251	−909
1600						−280	−1015
1800							−1178

Table 2 gives the observed effects for No. 8-gage Chromel P and Alumel of changes in immersion as outlined above. In the tests up to and including 1600 °F the effect is gradual and approximately regular. At 1800 °F and above the Alumel element exhibited an irregular effect, somewhat similar to that observed in the exposure tests, which became more pronounced as the heating temperature was increased. Fig. 20 illustrates the results for the Chromel-Alumel thermocouples.

V. Discussion of Results

As has been previously pointed out the materials were heated in an atmosphere of clean air. Furthermore, the depth of immersion of the materials in the furnace was constant throughout each exposure test. Direct application of the results obtained must be limited to cases where these conditions prevail.

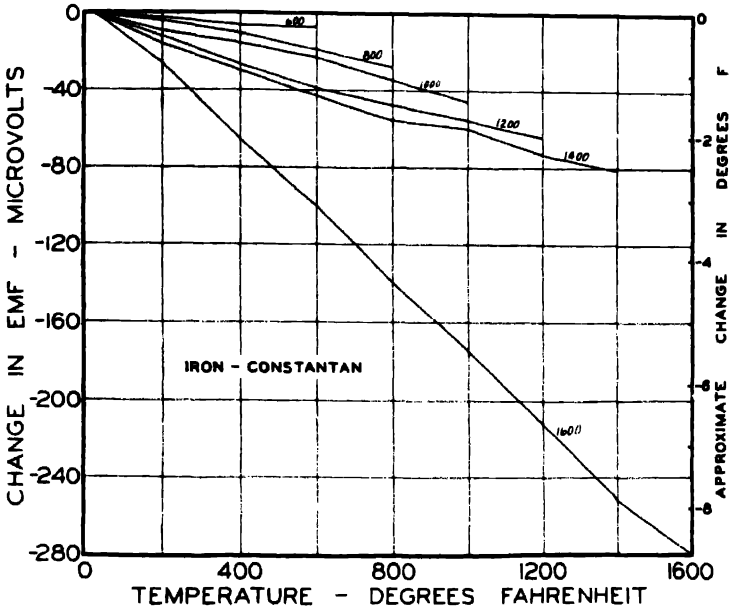

FIG. 19. Changes in the indications of No. 8-gage iron-constantan thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours in air at the temperatures indicated on the graphs.

From the observations reported it is seen that long-time exposure of a Chromel-Alumel thermocouple to high temperatures causes the emf corresponding to a given temperature to increase, or the temperature corresponding to a given emf to decrease. The effect on an iron-constantan thermocouple is just the reverse.

Failure of a Chromel-Alumel thermocouple (No. 8-gage) occurred within the 1000-hour heating period only in the test at 2200 °F. In this case an open circuit was indicated after 300 hours, and examination of the sample showed that the metal forming the welded junction and the individual wires for some distance from the welded junction were oxidized nearly through.

The 1000-hour heating periods at 2000 and 1800 °F for No. 8-gage Chromel P and Alumel also produced appreciable oxidation of the materials. In the test at 2000 °F the diameter of the wires after the oxide was removed was 2.3 mm for the Alumel and 2.6 mm for the Chromel P, as compared to 3.3 mm for the original diameters. For the test at 1800 °F the diameter after removing the oxide was 2.6 mm for the Alumel and 3.1 mm for the Chromel P. In the tests at 1600 °F and below the oxidation had not materially decreased the diameter of the wires.

Table 2. Changes (in microvolts) at Various Temperatures Caused by Decreasing the Depth of Immersion Three Inches after Heating in Air at the Temperatures Indicated for 20 Hours.

Calibration Temp. (°F)	Heating Temperature (°F)								
	600	800	1000	1200	1400	1600	1800	2000	2200
					Chromel P				
200	2	4	5	12	10	13	− 1	− 7	− 7
400	5	9	8	21	25	24	+ 1	−12	− 35
600	10	18	19	31	35	36	4	−14	− 50
800		31	30	36	45	45	10	−16	− 49
1000			40	41	54	57	13	−21	− 52
1200				49	59	71	31	−32	− 53
1400					65	79	48	−28	− 81
1600						86	68	−29	−103
1800							95	−28	−130
2000								−18	−158
2200									−176
					Alumel				
200	1	1	2	− 2	− 2	− 3	− 5	−13	− 31
400	3	2	1	− 3	− 4	− 6	−26	−59	−128
600	9	7	− 1	− 6	− 6	− 8	−35	−89	−193
800		10	− 4	−12	−11	− 9	−25	−73	−159
1000			+ 1	−17	−17	−10	−10	−46	−134
1200				−17	−25	−12	−13	−33	− 78
1400					−25	−15	−21	−39	− 86
1600						−17	−32	−54	−110
1800							−45	−74	−157
2000								−102	−214
2200									−281
					Chromel-Alumel				
200	1	3	3	14	12	16	4	6	24
400	2	7	7	24	29	30	27	47	93
600	1	11	20	37	41	44	39	75	140
800		21	34	48	55	54	35	57	110
1000			41	58	71	67	23	25	82
1200				66	84	83	43	1	25
1400					90	94	69	11	5
1600						103	100	25	7
1800							140	46	27
2000								84	56
2200									105

The exposure tests on No. 8-gage iron-constantan thermocouples showed failure of the materials within the 1000-hour heating time for the tests at 1600 °F and above. Failure occurred after 12 hours at 2000 °F, after 28 hours at 1800 °F, and after 300 hours at 1600 °F. The No. 18-gage iron-constantan thermocouple failed after about 500 hours at 1400 °F, whereas the No. 8-gage thermocouple remained serviceable throughout the 1000-hour test at 1400 °F. However, at the conclusion of the test, the diameter of the No. 8-gage materials had been reduced to about 1/10 of their original value.

A summary of the changes observed for Chromel-Alumel, iron-constantan, and Chromel-constantan thermocouples produced by long-time exposure to various temperatures is given in Table 3. The values for Chromel-constantan were obtained indirectly by combining the changes in the individual elements. Though the changes in both Chromel P and constantan are considerably larger than those of the completed thermocouple, the direction is such that the changes counteract each other, so that the change in a Chromel-constantan thermocouple is small. The life of this thermocouple is limited by that of the constantan element.

The relatively large changes in calibration which were observed for Chromel-Alumel thermocouples at 400 and 600 °F after the couples have been exposed to temperatures of 1600 °F and above are not as serious as may at first appear. When a thermocouple is used for accurate measurement of temperatures of 1600 °F or above it is seldom required that this same couple be used for accurate measurement at temperatures as low as 400 or 600 °F. Therefore the relatively large changes at these lower temperatures are of no great importance. A thermocouple which is to be used for accurate measurements below 1000 °F should not be exposed to the higher temperatures. If this procedure is followed the relatively large changes at 400 and 600 °F will be avoided.

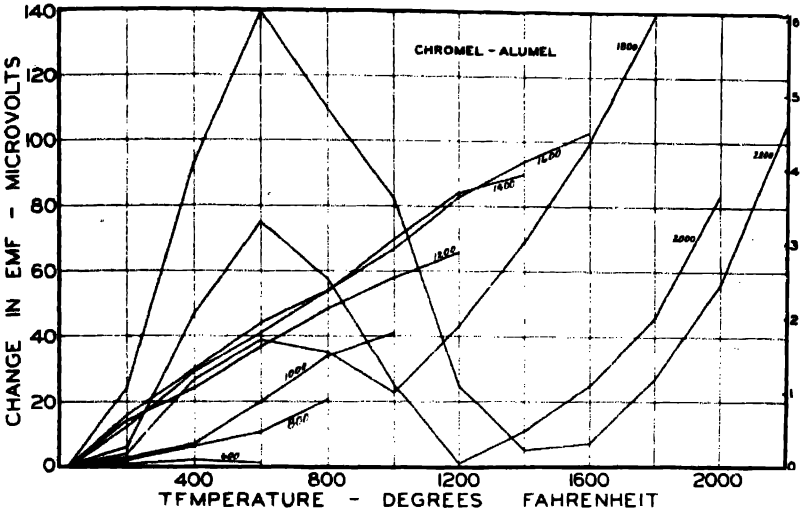

Fig. 20. Changes in the indications of No. 8-gage Chromel-Alumel thermocouples due to a 3-inch decrease in immersion after the couples had been heated in air for 20 hours at the temperatures indicated on the graphs.

Table 3. Changes in the Calibration of Base-metal Thermocouples Heated in Air (Electric Furnace).

	Chromel-Alumel		Iron-Constantan		Chromel-Constantan	
Exposure Temp. (°F)	Exposure (hrs)	Maximum Change (°F)	Exposure (hrs)	Maximum Change (°F)	Exposure (hrs)	Maximum Change (°F)
800	1000	< 1	1000	< 1	1000	<1
1000	1000	< 1	1000	< 1	1000	<1
1200	1000	+ 2	1000	− 4	1000	−1
1400	1000	3	800	− 7	1000	−2
1600	1000	5	100	−10	100	−4
1800	1000	8	28	−18		
2000	1000	19	8	−19		
2200	200	21	....	....		

The results on the immersion tests emphasize the importance of never decreasing the depth of immersion of a thermocouple after it has once been placed in service. The practice of using a single base-metal thermocouple for high-temperature measurements in a number of different installations should be avoided. It is even difficult to obtain consistent and accurate results by using a thermocouple in a single installation if the couple is withdrawn and replaced between periods of service. The results obtained by removing a used base-metal couple from an installation to determine the corrections to the original calibration by testing it in a laboratory furnace are unreliable. The temperature gradients in the two furnaces usually differ widely, and hence the results will not be applicable to the actual service conditions. If it is practicable by any means to remove the inhomogeneous portions of the thermocouple from the temperature gradient, then the original calibration of the couple is applicable.

Discussion

W. A. Gatward, Chief Engineer, Hoskins Manufacturing Co., Detroit, Michigan: Mr. Dahl has very carefully limited his statements regarding this experiment to cover oxidizing conditions only. He has found under such conditions that generally, Chromel-Alumel thermocouples will produce higher emfs after use. In practice it is usually found that the opposite is true, that is, that when changes develop, the couples usually "read low." The tendency to read low will be caused by reducing gases which are likely to be present even under the best protection. We might say then, that the tendency to read high as caused by oxidation will in many instances be partially, wholly, or excessively compensated by the tendency to read low, as caused by gas contamination.

Mr. Dahl is dealing with very small changes, some of them equivalent to fractions of a degree. There are some instances where the data are not consistent, as for instance where he gets more change in 100 hours than in 200 hours, or where his curves cross over. I know when trying for such accuracy as this, that errors are apt to creep in, and there are two questions I would like to raise concerning his technic.

Asbestos wool was used to plug up the end of the test furnace. That has been known to cause errors if a reducing gas is driven off from the wool and into the furnace at a high enough temperature. The exact limitations of the use of asbestos wool are not known, so it should be used with caution.

The other point involves temperature gradients. With the test wires and the platinum couple all welded together it is possible to take perfectly good readings while the temperature is changing. However, the effect of the temperature gradient is such that plenty of time should be allowed for the temperature gradient to reach its equilibrium. For a given design of furnace there will be a very different temperature gradient for each temperature used, and it takes considerable time for this gradient to establish itself. Too rapid manipulation of the temperature of the furnace is suggested as a possible cause of some small discrepancies.

Possibly the accuracy of the potentiometer is not consistent with the accuracy of the control of conditions in the test and part of the data may be out of "accuracy balance."

It is quite evident that temperature gradient, a necessary evil, is one of the important considerations in the use of thermocouples. Very few people are familiar with what goes on in the "zone of uneven heating" or, the "temperature gradient," and I believe a more thorough discussion of the problem would be in order in this paper.

In discussions of this sort we use terms which we would be hard-put to define. For instance, inhomogeneity. Now we have a pretty good conception of its opposite, homogeneity, because a piece of wire is homogeneous if a temperature gradient does not set up local emfs or "parasitic emfs." It is pretty safe to say that such a wire is very uniform as to composition and physical state.

If a wire is such that parasitic emfs *are* set up by a temperature gradient, then we say that it is inhomogeneous without knowing wherein inhomogeneity lies. Maybe the hottest part of the wire has lost some small part of its chemical ingredients. Maybe some surface oxide has been reduced permanently or temporarily. Maybe the physical state or the crystal form (as in the case of nickel) has been temporarily or permanently disturbed so that a parasitic emf could "come and go," depending on the temperature at the moment.

These are mentioned just as possibilities, to show that inhomogeneity may be one or several things all at the same time. Whatever it may actually be, it is the temperature gradient acting on the non-uniform wire which causes parasitic emfs which add or detract from the total couple emf.

It is one thing to age a couple wire when we heat the whole wire to some high temperature, as for annealing or stabilizing purposes. But aside from that, each couple in use is submitted to an ageing process, not at one temperature but at many temperatures along its length. A couple must reach from the high-temperature zone out to room temperature and it must pass through a temperature gradient. Hence, the couple in use is not aged uniformly at all.

Notice that in Mr. Dahl's curves, Figs. 1 to 4 inclusive, where the ageing temperature only reaches 1400 °F, the changes are more or less uniform and proportional to time and temperature. Those in Figs. 5 to 8 inclusive are quite different with decided "humps" in the Alumel curves at 400 to 500 °F.

It must be borne in mind that a couple which is aged at 1400 °F must pass through a continuous gradient clear to room temperature just as does the couple which is aged at 1600 °F. And still the couple aged at 1600 °F will exhibit the "hump" at 400 to 500 °F while the one aged at 1400 °F will show no "hump."

It is hard to believe that a hot-end temperature of 1600 °F would *in itself* cause an effect different from 1400 °F. It is pretty certain that if two wires were completely aged (the whole length) at 1400 and 1600 °F they would behave in the same way as to the hump. Knowing the peculiarities of nickel at 400 to 500° F, and knowing that Alumel is 95 per cent nickel, we would expect that the hump in the Alumel curve must be caused by a temperature at around 400 to 500 °F, which can only occur in the temperature gradient.

Fig. 21 has been drawn to represent a possible temperature distribution in a test furnace. Curve A could be the temperature of a wire being aged at 2000 °F. It will have one end in a uniform zone, L_5, and the other end at room temperature L_1. The remaining part represented by L_2, L_3, and L_4 will be in the gradient zone. Now forget L_2 and L_4 for a moment and think of L_3 as representing the inhomogeneous wire which has been aged at many different temperatures along its length. One end could be at 1500 °F, and the other end could be at 500 °F. If L_3 is inhomogeneous then 1500° at one end and 500° at the other end would cause a parasitic emf, and it might add to or it might subtract from the emf of the whole wire against platinum.

Now after the aging at 2000 °F, suppose the temperature of L_5 is dropped to B, or to 500 °F. We know that the two ends of L_3 will also be lowered say to 400 and 200 °F, and any parasitic emf, if present, will be of different degree and might even be of different sign.

Isolating L_3 and making the foregoing assumptions, we can see that the temperatures involved could be those which would affect the Alumel. While this is all speculation and does not suggest any cure for the effect of a temperature gradient, it does suggest an experiment which might explain the hump.

A furnace could be made up with 3 controllable zones, one representing the section L_5 and the two others which could be controlled at lower temperatures and which would represent the two ends of L_3. Then a length of wire could be welded into the Alumel wire, an insert several inches long, and of material having a decidedly different emf from the Alumel wire. This insert would then represent L_3.

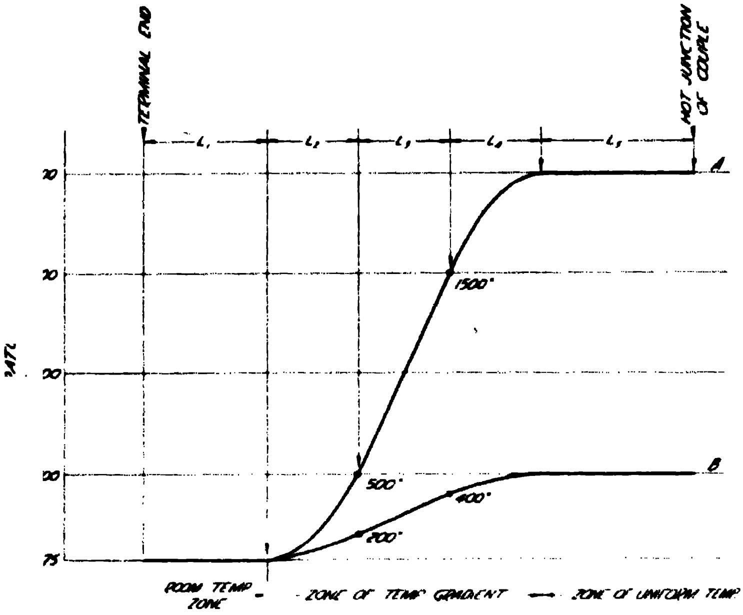

FIG. 21. Possible temperature distribution in test furnace.

Now a test could be run with selected temperatures for the ends of L_3 and a selected temperature for L_5. Then L_5 could be changed, but the difference in temperatures at the ends of L_3 could be kept the same, so that any parasitic emf in L_3 would be the same regardless of the temperature of L_5. This sort of experiment would contribute something to the explanation of the hump in the Alumel curves.

Time Rate of Change When a Chromel-Alumel Couple is Not Disturbed and is Held at One Temperature

When accurate temperatures must be measured over a long time, the couple should be checked periodically "in place," that is, not disturbed in any way. There are data in Figs. 1 to 8 inclusive which will tell what to expect in changes of emf with time. These data can be taken from Figs. 1 to 8 at the extreme right-hand end of the curves. Fig. 22 has been prepared in this manner. In some cases the curves cross over and it is not possible to identify all of them. When this occurs, the average of the group is used. It occurs only where the changes are very small, a degree or so.

Mr. Dahl's paper may at first be alarming to users of Chromel-Alumel couples. Many of them depend implicitly on check couples which are used at many temperatures and immersions.

In discussing the use of couples the expected accuracy should always be stated so that a user may decide just how he may operate his couples to attain the desired accuracy.

Mr. Dahl has carefully defined the conditions of his experiments as oxidizing. He has made some valuable suggestions in the use of Chromel-Alumel couples. However, it seems if he could combine his recommendations with his statements defining the accuracy expected, then his recommendations would have more practical use. If such accuracy cannot be conveniently defined, then he might head his list of recommendations with the statement that "extreme accuracy requires the following precautions." Such precautions selected from various paragraphs could then be summarized as follows.

(1) A couple which is used for measurements below 1000 °F should not be exposed to higher temperatures.

(2) A Chromel-Alumel couple which is used up to 1600 °F or higher should not be used for accurate measurements below 800 °F.

(3) The depth of immersion should not be changed from the original, and above all it should not be decreased.

(4) Any thermocouple should be checked if possible in place, *i.e.*, undisturbed in any way.

Reply

The asbestos wool used to close the ends of the furnace tube did not become heated to temperatures sufficiently high to disturb the oxidizing atmosphere within the tube. The wool was loosely placed against the ends of the tube. This permitted a relatively easy passage of air into the tube and if any foreign gases were liberated from the asbestos wool they would be so diluted with an excess of air that their effect would be negligible.

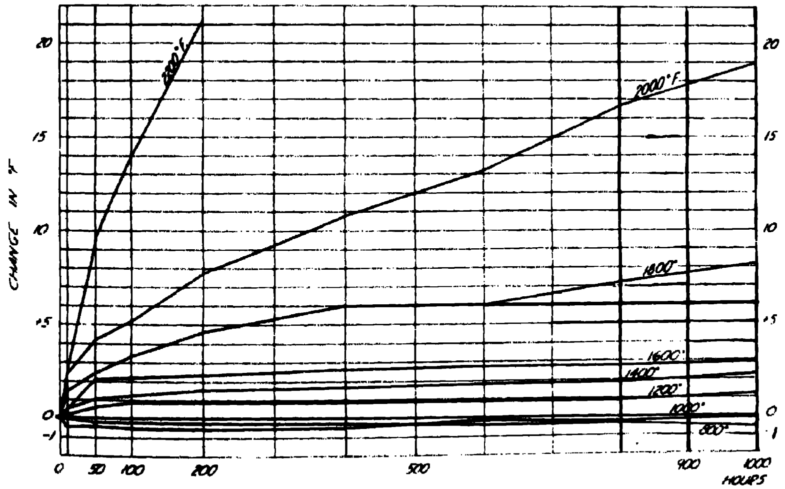

Fig. 22. Rate of change for Chromel-Alumel couples left undisturbed and aged at temperatures shown.

The time allowed for the temperature gradients in the test wires to become established after the furnace reached the desired steady temperature was about 15 minutes for temperatures up to 1200 °F and about 10 minutes for temperatures above 1200 °F. Moreover, the furnace temperature was changed slowly in passing from one point to the next. The emf of the test wires against platinum at the time the observations were recorded showed no variation with time when the temperature was maintained constant. This would indicate that equilibrium conditions had been reached.

The over-all accuracy of the measurements at any given temperature, including the uncertainties in the potentiometers, the standard thermocouple, and the platinum reference wire, is estimated to be within 0.5 °F.

Discussion

A. H. Salerno, Hyatt Bearings Division, General Motors Corporation, Harrison, N. J.: Commenting on Mr. Dahl's paper from the viewpoint of the pyrometer user, I wish to say that in the selection of the type of material to be used for base-metal thermocouples in commercial application, it is necessary to know the conditions under which the wire will be used. Characteristics are influenced by type of atmosphere, whether oxidizing, neutral or reducing, and by time and temperature. Having decided upon the particular conditions, it is of extreme importance to consider the economies involved. It is well known that different types of couples will have a variable life depending upon the amosphere in which they are used. The comparative cost per hour of service might justify the use of the less expensive of two wires, even though it is necessary to change couples more frequently. The fact that a couple must be taken out of service to avoid errors with continued use before failure occurs does not necessarily indicate an unsatisfactory type of material. Frequency of changing couples can be adjusted to avoid using them beyond the point of instability.

The atmospheric conditions encountered in the tests reported on by the author were undoubtedly quite strongly oxidizing. This condition is not always met with in practice.

In cases where difficulties might arise from using couples in a strongly oxidizing atmosphere, it is often advantageous to pack them so as to exclude as much oxygen as possible and thereby lengthen their service life.

Our practice in the use of iron-constantan thermocouples is to replace with new couples at regular stated intervals, regardless of their apparent condition. The length of time allowed in service depends on the temperature of operation. This is given below for I-C couples.

Temperature of Use	Period of Use
1700 °F	672 hours
1450–1550 °F	360 hours
300–800 °F	8760 hours

These periods are for 24 hours per day, 7 days per week. The 1700 °F-couples are packed with T.C. packing, while the others are in unpacked tubes. This accounts for the apparent discrepancy between the 1700 °F and the 1450-1550 °F time of use figures. The time of service does not indicate failure but has a large factor of safety, since the couples are inexpensive and the parts being heat-treated are valuable.

Since we have never made life tests on any thermocouple wire we are not in a position to offer comments on the stability under these conditions, other than the data given above.

G. C. Stauffer, Driver-Harris Co., Harrison, N. J.: The author of this paper should be complimented on the work done with the very desirable object of collecting information on the life of base-metal thermocouple materials.

Attention should be called to the fact that the results in this paper indicate the effect of definitely oxidizing conditions on base-metal thermocouple elements. It appears quite probable that the test conditions were considerably more strongly oxidizing than is met with in the industrial applications of base-metal thermocouples.

The results on constantan indicate what happens when it is exposed to an unknown concentration of oxygen at elevated temperatures for various periods of time. The heretofore unpublished data below indicates that the oxygen concentration in the atmosphere is more significant than the time factor. The life of any couple depends on the atmosphere. Strongly oxidizing atmospheres on an unprotected iron-constantan couple will cause rapid deterioration at temperatures over 1600 °F. It is well known that reducing atmospheres are equally destructive to some other types of base-metal couples.

In 1934 the National Bureau of Standards made some routine commercial calibrations against platinum of keyed samples submitted by the alloy manufacturer. Nine samples from one coil of No. 8 wire were taken. The coil had been given a commercial anneal at 1450 °F for 4½ hours in a closed pot. A neutral or slightly reducing atmosphere was maintained.

Of the nine pieces, one sample received no additional heat treatment. Four of the remaining samples were heated for three hours in pure hydrogen, the other four were placed in steel tubes packed with Aloxite and sealed on the ends with fireclay. This was termed an oxidizing anneal. The eight samples were then heated for three hours to the temperatures indicated.

Table 4. Heat Treatment.

Sample Number	Time (hrs)	Temp. (°F)	Atmosphere	Emf vs. Pt 27 at 1500 °F (mv)	Net Change from No. 1 (µv)
1	.		....	35.53	00
2	3	1400	Hydrogen	35.55	− 20
3	3	1600	Hydrogen	35.58	− 50
4	3	1800	Hydrogen	35.60	− 70
5	3	2000	Hydrogen	35.59	− 60
6	3	1400	Oxidizing	35.47	+ 60
7	3	1600	Oxidizing	35.52	+ 10
8	3	1800	Oxidizing	35.03	+500
9	3	2000	Oxidizing	34.97	+560

It would be expected that, if the oxidizing conditions were uniform for samples No. 6 and No. 9 inclusive, the change in microvolts would be consecutively greater with higher temperatures of treatment. It should be noted that this is not the case, which indicates that the oxidizing conditions were not uniform.

Comparing the tests in oxidizing atmospheres given in Table 4 with the figures given by Mr. Dahl, it will be seen that Sample No. 6, for example, shows a greater change than is given by Mr. Dahl in Fig. 14 for the same temperature but a longer period The change on sample 7 for the oxidizing atmosphere at 1600 °F compares approximately with the data given by Mr. Dahl in Fig. 15.

A recent test to show the effect of exposure of constantan to severe oxidizing conditions for three hours at 1700 °F showed a change of 1650 microvolts when checked at a temperature of 1500 °F.

The results on the samples in the reducing atmospheres all having increased slightly, it is logical to assume that a strictly neutral atmosphere would have caused no change. Thus variations in atmospheric oxygen content will cause changes as high as 1650 microvolts at a 1500 °F test temperature when the wire is heated for only three hours. This indicates the necessity of knowing the condition of oxidation of the atmosphere in contact with the couple.

Commercial practice has indicated throughout the years that properly installed couples do not deteriorate at the rate shown by Mr. Dahl. Actual values fall between the ideal of no change, in the reducing atmosphere, and the rapid change shown under oxidizing conditions.

The amount of increase in emf after heating in reducing atmospheres has been determined to depend on the previous history of the sample. Properly melted and annealed samples show only slight changes. A piece which has been severely oxidized may be restored to its original value by heating in hydrogen at a temperature of 1850 °F for from 15 minutes to an hour or more. For example, the previously mentioned piece which changed 1650 microvolts after heating for 3 hours at 1700 °F in an oxidizing atmosphere and which had scaled off 0.005″ was fired for one hour at 1820 °F in an atmosphere of pure hydrogen.

Original value	35,500 μv vs Pt 27 at 1500 °F
After oxidizing at 1700 °F	33,850 μv vs Pt 27 at 1500 °F
After hydrogen heating at 1820 °F	35,575 μv vs Pt 27 at 1500 °F

The change is not due to the reduction of the surface oxide, since if the surface is completely removed by pickling or machining, the emf of the wire does not return to the original value until it has been fired in hydrogen.

It is apparent from this that the core of the metal in some way takes up oxygen, which definitely lower the emf of the wire. This effect on the emf is neutralized, and the oxygen is presumably removed when the wire is heated at high temperatures in an atmosphere of hydrogen.

It is obvious from the foregoing that when iron-constantan thermocouples are used it is desirable to use tight protection tubes and limit infiltration of air to the minimum.

Reply

I do not agree with Mr. Stauffer's statement that "the results on constantan indicate what happens when it is exposed to an unknown concentration of oxygen at elevated temperatures for various periods of time," because the atmosphere in which the materials were heated was that of clean air and therefore of known and constant oxygen content. The rate at which oxygen was consumed in the oxidation of the materials during heating was not great enough to change the oxygen concentration within the furnace appreciably since an excess of air was present at all times.

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Platinum and Pyrometry

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Baker & Company, Newark, N. J.

The relation of platinum to pyrometry is one of fundamental scientific importance. Platinum serves as the means of interpolation between the fixed temperatures that in practice determine the standard temperature scale.[1] Below 660 °C it is the resistance thermometer that defines the intermediate temperatures for precision measurements; between 660 and 1063 °C, it is the thermocouple of C.P. platinum and of the alloy of platinum with ten per cent rhodium.[2] It should be noted that these ranges of temperature definition do not coincide with the working ranges of the two instruments.

The adoption of platinum for fundamental use in pyrometry is the result of the unusual properties of the metal—high melting point, chemical stability, resistance to oxidation, and availability in pure form. Any metal to be used for pyrometric measurements should be capable of absolute reproduction from lot to lot and should be stable in calibration throughout its lifetime. Of course no metal can meet such requirements, but platinum meets them more closely than any other. For resistance thermometers the very purest of platinum is required in order to secure a high, uniform value for the temperature coefficient of resistance. The metal is always supplied by the refiner in the form of wire, and the production of the complete resistance thermometer is left to the user or to the instrument maker. For thermocouples, C.P. platinum and a platinum alloy containing either ten or thirteen per cent rhodium are used. The couple with the ten per cent alloy is the more common

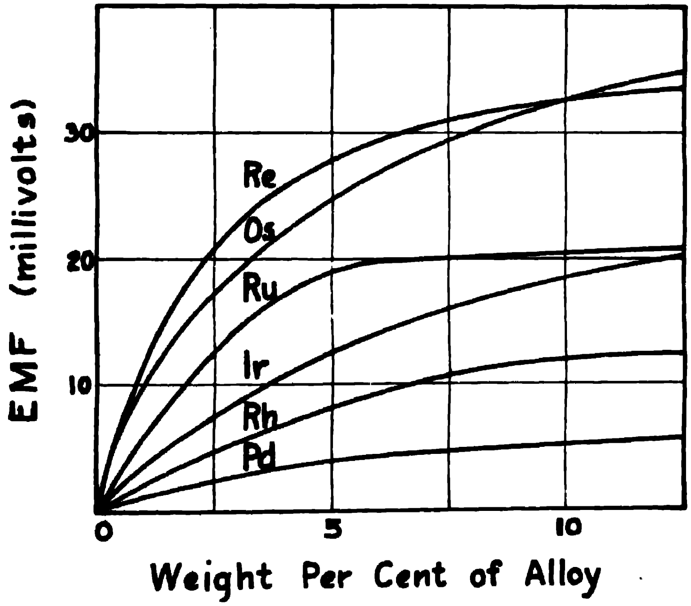

Fig. 1. Influence of added elements upon the thermal emf of platinum at 1200 °C.

in this country and is considered standard, although that with the thirteen per cent alloy is in common commercial use. A practical advantage of the ten per cent alloy is its lower cost. The range of satisfactory service of the resistance thermometer extends to 800 ° or 900 °C; that of the thermocouple to 1300 °C, and even to 1500 or 1600 °C, under special conditions.

The platinum-rhodium couple, as shown by Fig. 1, produces a relatively small thermal emf as compared with some of the other possible noble-metal combinations. The couple has been widely adopted, nevertheless, because of its stability. Other noble-metal alloys have been suggested for thermocouples, sometimes to obtain larger emfs and sometimes to obtain higher limits of use; but these substitutes have never been widely adopted because they change calibration too rapidly, and some have poor mechanical properties. The couple of iridium against iridium 10 per cent rhodium has been used for temperatures above the limits of the platinum-rhodium combination. Its elements have melting points 600 to 700 °C higher than those of the components of the usual couple. It has serious disadvantages in that it is insensitive, subject to rapid change of calibration, and brittle. Another couple which has been studied is that of the alloy of platinum with eight per cent rhenium against platinum.[3] This couple has a high thermal emf, but is subject to a more rapid change of calibration than the platinum-rhodium couple. A modification has been developed in which the eight per cent rhenium is replaced by 4.5 per cent rhenium and 5 per cent rhodium in order to increase the stability. For use at temperatures below those customary with platinum thermocouples, under conditions where chemical inertness is desired, as well as a high emf, a noble-metal combination has been employed that consists of platinum or platinum 10 per cent rhodium against an alloy of 60 per cent gold-40 per cent palladium. Some of the physical properties of platinum and of the ten per cent rhodium alloy are shown in Table 1.

Table 1. Physical Properties of the Components of the Platinum-Rhodium Thermocouple.

Property	Platinum	Platinum 10% Rhodium
Resistivity (0°C)	9.8 microhm cm.	18.3 microhm cm.
Temp. Coef. of Resis.		
0- 100 °C	.0039	.0018
0- 500	.0036	.0017
0-1000	.0033	.0016
0-1400	.0030	.0015
Melting Point	1773 °C	1830 °C (solidus)

The reproducibility of platinum for pyrometric purposes depends upon the purity of the original sponge and upon the care used in melting and fabricating the metal. Control of the C.P. platinum and of the platinum-rhodium alloys after fabrication is by means of thermal emf. The standards used are based on the C.P. platinum standard maintained by the Bureau of Standards in the case of platinum, and upon calibrations of platinum-rhodium couples made by the same institution in the case of the alloys. In commercial practice deviations of +20 microvolts or less at 1200 °C are regularly obtained. Measurements at several temperatures verify the correct shape of the emf-temperature curve. Wires of as nearly equal deviations as possible are used in making a couple, and consequently the error of a new thermocouple is considerably less than the 3 °C which is the usual guarantee.

A determination of the magnitude of the impurities that produce the small deviations observed in the thermal emf of C.P. platinum can be obtained only from physical measurements, because chemical and spectrochemical determinations are not sufficiently sensitive. Alloys of platinum containing ten per cent of rhodium and of iridium, respectively, have been diluted down to 0.001 per cent by steps of factors of ten, and the thermal emf at 1200 °C measured for each of the alloys. From the experimental curves the smoothed values of emf given in Table 2 were obtained.

Table 2. Thermal Emf of Platinum Alloys of Rhodium and Iridium.

Weight, %	Thermal Emf at 1200 °C vs. Platinum Standard (Microvolts) Rh	Ir
0	5	5
.001	20	35
.002	35	60
.003	50	90
.004	70	115
.010	135	210

The values of the thermal emfs of the 0.001 per cent alloys were of the general order of C.P. platinum, indicating that C.P. platinum, to judge from this test alone, is of the order of 99.999 per cent pure. If all impurities caused approximately the same thermal emf as rhodium, the tolerance in C.P. platinum would correspond to about 0.001 to 0.002 per cent of impurity. These figures are presented merely to indicate the order of the phenomena and should be considered as only approximate. In particular, the thermal emf cannot be used alone as a measure of the chemical purity of a metal, not only because this property is affected differently by different impurities, but because it is not affected by those impurities which have not entered into solid solution with the metal.

It is customary before using or calibrating thermocouples to anneal them to remove strains and to stabilize the thermal emf. Preferably such conditioning should be done at temperatures above those that will be encountered in service, but caution is necessary because too vigorous treatment may affect the calibration. This may be of no consequence when the couple is to be calibrated later, but it is important under circumstances where interchangeability of couples is required. We find treatments at 1200 to 1300 °C to be satisfactory for stabilization, and at higher temperatures we prefer to anneal for only five to ten minutes. The Bureau of Standards has adopted the procedure of annealing all platinum-rhodium couples for one hour at 1450 °C.[4]

Table 3. Influence of Temperature on Thermal Emf of C. P. Platinum.

Temperature (°C)	Thermal Emf at 1200 °C (Microvolts) After 5 minutes	After 1 hour at 1450 °C
600	−1	+3
800	−1	3
1000	−2	3
1100	−1	1
1200	0	0
1300	+1	1
1400	1	0
1500	2	2

The continued heating of C.P. platinum in air at elevated temperatures in our experience always produces a slight reduction in the thermal emf, presumably through both the release of strains and the oxidation of impurities. However, phenomena have been observed which are not in agreement with this tendency. In measurements made at the Bureau of Standards,[5] several lengths of wire were heated for five minutes at different temperatures, and later reheated for one hour at 1450 °C. As shown in Table 3, increased temperature of treatment increased the thermal emf and decreased the apparent purity of the platinum. A similar apparent decrease in the purity of C.P. platinum has been observed in measurements of electrical resistance at low temperatures.[6] The ratio of resistance at 20 °K to that at 273 °K, designated as r_{20}, was found to increase as the temperature of preliminary annealing increased, as shown in Table 4. In this case a low value of r_{20} indicated a high degree of purity. It will be noticed that the result of an apparent decrease of purity in each case depends upon an electrical measurement. The deviations observed may have been the result of physical changes; but possibly the explanation may lie in the decomposition and subsequent solution of inclusions, such as oxides, which had been present previously in an undissolved state and had not been revealed by the electrical tests; or the explanation may lie in the absorption and rejection of a constituent of limited solubility, such as oxygen.

Table 4. Influence of Temperature of Annealing upon the Resistivity of Platinum.

Heating Time (min)	$r_{20} \times 10^3$			
	750 °C	850 °C	1000 °C	1100 °C
5	6.0	6.0	6.2	6.6
20	6.0	6.0	6.2	6.7

The life of a thermocouple in use, particularly its maintenance of calibration, is subject to many factors and is difficult to predict. A thermocouple should always be used under oxidizing conditions; yet even under such conditions there are several factors that cause it to go off calibration in time. In the first place, there is the possibility at high temperatures of slow absorption of impurities present in the atmosphere. Secondly, there is a slow volatilization of the couple, depending in rate upon the temperature, which produces a change of calibration as a result of unequal rates of volatilization of the platinum and of the rhodium. A third source of difficulty is important only with the use of small immersions of the couple or with determinations of point temperatures; this is the slow diffusion of rhodium from the alloy to the platinum at the hot junction. These three errors are all, to greater or less extent, volume-sensitive in that wire size, or volume, is of importance in determining the time required to make the change in composition significant. In general, wire of 0.0236 inch (0.6 mm) diameter is used as the best compromise between cost and service. Wire size, as such, however, does not appear to influence the thermal emf of a couple, experience being that, down to diameters of 0.0004 inch, which is about as fine as wire can be bare-drawn, the emf is independent of size.

Care must be taken with platinum with regard to the materials that come into contact with it. Even under oxidizing conditions, at very high temperatures certain oxides in contact with it are partially reduced to metal, which thereupon alloys with the platinum.[7] Under oxidizing conditions a couple should, therefore, be in contact with only stable oxides, if change of calibration from absorption of impurities is to be held to a minimum. Experience long ago dictated the use of inert oxides for commercial insulation and protection tubes.

Unquestionably the most dangerous condition of all for a platinum thermocouple is direct use in a reducing atmosphere. Otherwise harmless oxides decompose and the resulting metals and metalloids combine with the platinum. Some may only change the calibration of the couple, but others will reduce the fusing point sufficiently to destroy the couple completely. Platinum at elevated temperatures should never be used unprotected under reducing conditions if contamination is to be avoided. It should always be protected by a gas-tight tube, care being taken that the latter is not in service too long, because eventually it becomes porous as a result of absorption of the glaze by the body.

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Factors Affecting the Life of Platinum Thermocouples

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The useful life of a platinum thermocouple can be reckoned from the time it is put into service until it is removed because of being off calibration beyond the allowable tolerance. Platinum thermocouple wire available from several sources in this country is of very high purity, and in order to maintain accuracy and prolong the useful life of the thermocouple, it is the problem of pyrometer users to retard physical and chemical changes of the thermoelements as much as possible. It is generally understood that the thermocouple must be given the greatest possible protection against most furnace gases. Fortunately for this purpose primary protection tubes are obtainable on the American market which are satisfactory for most installations. The proper selection of pyrometer tubes varies with individual conditions and will not be considered here. This paper will be confined to a discussion of deteriorating influences within the primary tube itself.

When a platinum, platinum-rhodium thermocouple is put into service, changes begin to occur which alter the homogeneity and calibration of the thermoelements. The platinum element tends to become more positive, and indications are that the platinum-rhodium element becomes slightly positive and then negative. The causes of these changes are varied and differ under the many conditions of exposure.

Breathing of the tube is usually considered to be advantageous in order to maintain oxidizing conditions and prevent the reduction of certain oxides, particularly SiO_2 to Si, which is readily taken up by the thermoelements. However, breathing due to changes in atmospheric pressure, or temperature changes of the tube, might introduce foreign matter such as coal dust, metallic particles, or reducing gases.

In addition to contamination from without, at temperatures around 1100 °C and higher, the rhodium in the positive element volatilizes at a slightly greater rate than the platinum, and the original proportion of rhodium is reduced, thus lowering the emf of the couple. Some of the volatilized rhodium enters the platinum element and augments the effects of other forms of contamination tending further to reduce the emf of the couple. For this reason the platinum element should be protected from the influence of the platinum-rhodium element. Thus the double-bore insulating tube, which is ordinarily considered only as an electrical insulator, serves another very important purpose.

Another source of error in the platinum-rhodium element occurs when the temperature is around 500 °C. At these temperatures a dark coating of rhodium oxide often appears on the surface of the alloy wire. A homogeneity test will show the black section to be less positive, indicating a loss of rhodium. Inasmuch as the section thus affected will very likely be in a region of large temperature gradient, considerable error may be caused by this condition.

Platinum thermocouple wire, when received from the maker, has a relatively small grain size. As soon as it is put into service, grain growth proceeds until often after a period of time, depending on the temperature, the platinum wire will consist of a series of crystals occupying the entire cross-section of the wire. The rate of growth is less in the platinum-rhodium element. Apparently the grain size has little effect on the emf of the wire. What appears to be of great importance is the size and number of broad grain boundaries. Examination in our laboratory of thermocouples which had prematurely failed in plant installations almost invariably shows portions of the wire to have developed broad grain boundaries. The assumption is that a larger surface is exposed and contamination is more rapid; and in the case of the rhodium element, volatilization occurs at a greater rate. Wire which has been bent, twisted, or distorted in any way, particularly if it has been annealed at high temperatures, will, on further annealing, develop large grain boundaries For this reason thermocouples which are frequently moved about deteriorate more rapidly than those which are used in permanent positions.

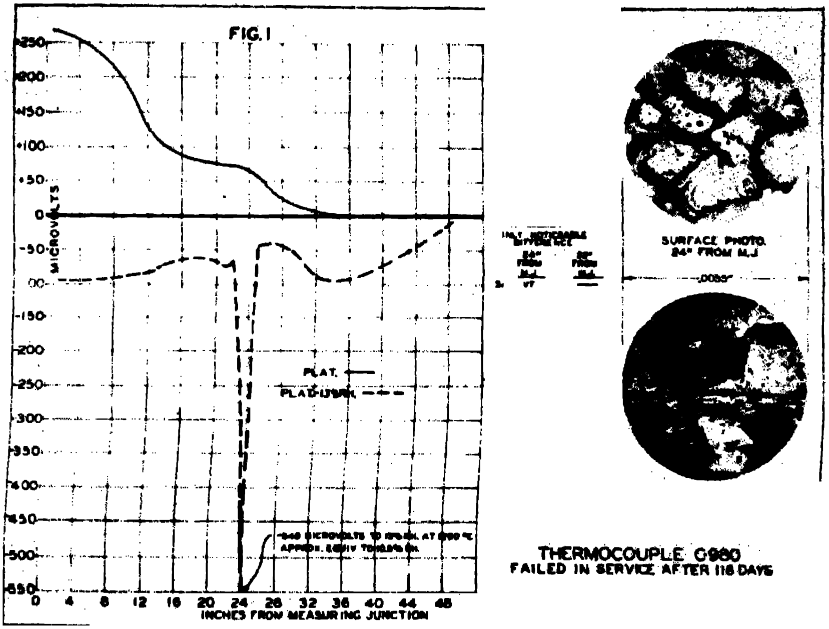


Fig. 1.

That the factors given above affect the life of platinum thermocouples has been concluded on the basis of tests made in the laboratories and plants of The New Jersey Zinc Company. The illustrations that follow show the results of several tests which were made in further study of some of these factors.

As an example of the effects of bends and twists in a thermoelement, Fig. 1 shows the homogeneity curve of a thermocouple which had failed in service after 118 days at 1290 °C. When the couple was removed from the furnace, it was found that at the junction of the two lengths of double-bore tubing, 24" from the measuring junction, the platinum-rhodium element was twisted into a very small loop. Apparently this was done at the time when the couple was assembled. The inhomogeneous section was very probably caused by this loop having been bent and exposed without the protection of the double-bore tubing. The photomicrographs show how the grain boundaries had increased in size as compared with a section

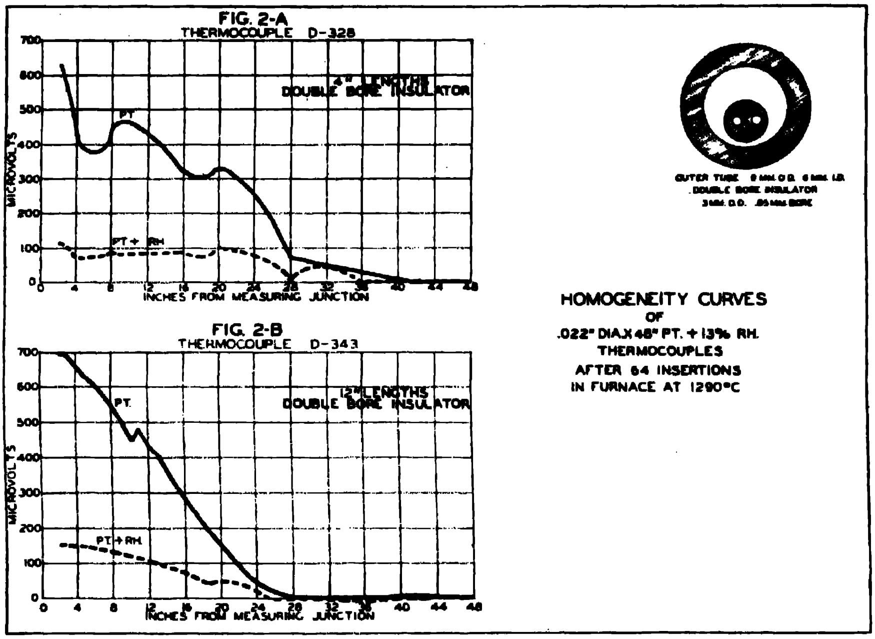


FIG. 2-A
THERMOCOUPLE D-328
4" LENGTHS
DOUBLE BORE INSULATOR
PT
PT + RH
MICROVOLTS
700
600
500
400
300
200
100
0
0
4
8
12
16
20
24
28
32
36
40
44
48
INCHES FROM MEASURING JUNCTION
FIG. 2-B
THERMOCOUPLE D-343
12" LENGTHS
DOUBLE BORE INSULATOR
PT.
PT. + RH.
MICROVOLTS
INCHES FROM MEASURING JUNCTION
OUTER TUBE MM. O.D. MM. I.D.
DOUBLE BORE INSULATOR
3 MM. O.D. .85 MM. BORE
HOMOGENEITY CURVES
OF
.022" DIA.X 48" PT. + 13% RH.
THERMOCOUPLES
AFTER 64 INSERTIONS
IN FURNACE AT 1290°C

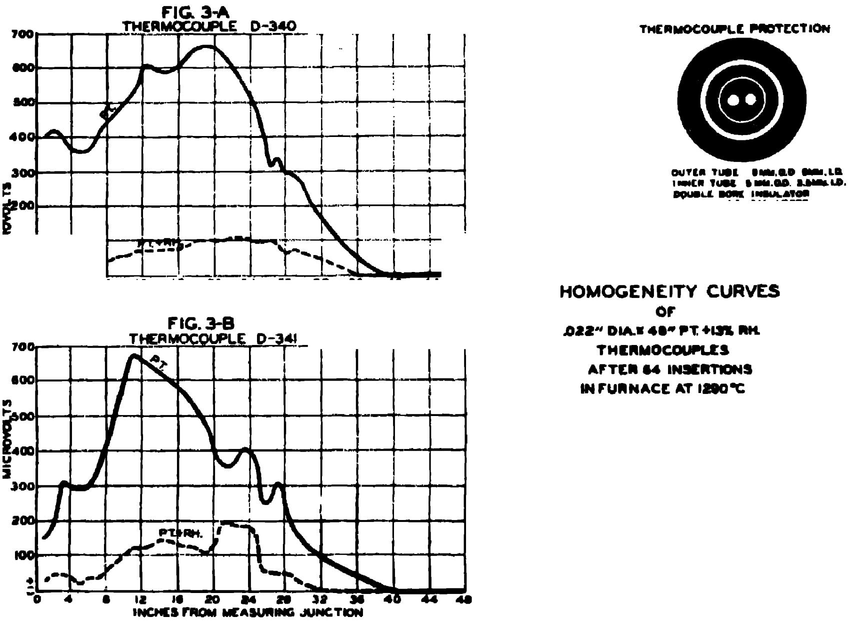


FIG. 3-A
THERMOCOUPLE D-340
PT.
PT. + RH.
700
600
500
400
300
200
MICROVOLTS
THERMOCOUPLE PROTECTION
OUTER TUBE MM. O.D. MM. I.D.
INNER TUBE MM. O.D. MM. I.D.
DOUBLE BORE INSULATOR
FIG. 3-B
THERMOCOUPLE D-341
PT.
PT. + RH.
MICROVOLTS
700
600
500
400
300
200
100
0
0
4
8
12
16
20
24
28
32
36
40
44
48
INCHES FROM MEASURING JUNCTION
HOMOGENEITY CURVES
OF
.022" DIA. x 48" PT. + 13% RH.
THERMOCOUPLES
AFTER 64 INSERTIONS
IN FURNACE AT 1290°C

FIG. 3.

8″ away. At the center of the loop the emf was found to be 548 microvolts negative to 13 per cent rhodium at 1350 °C. If the inhomogeneity was due entirely to the loss of rhodium, the element at this section would contain about 10½ per cent rhodium. The spectrographic analysis made on the 24″ and 32″ sections showed the only difference to be a very faint line of silicon, and it is believed that the decrease in the emf in the exposed and distorted section was caused by the loss of rhodium. The difference of the rhodium contents at these high percentages would not have been detected by the spectrographic analysis.

In an attempt to evaluate the effects of various kinds of protection, a number of tests were carried out with thermocouples made up with several different arrangements of double-bore and primary protection tubes. Exposure was made by inserting each thermocouple into a secondary pyrometer tube, the hot end of which was at 1290 °C. After the thermocouple reached equilibrium it was withdrawn and transferred to another position in the furnace. This was repeated 64 times for each thermocouple. The results were interpreted from the homogeneity measurements made every 2 inches throughout the entire 48″ length. Fig. 2A shows the homogeneity curve of a thermocouple which had been insulated with 4″ lengths of double-bore tubing. Both elements developed large inhomogeneities in the positive direction, indicating that some form of contamination had taken place. The shape of the curve indicates that the effects were greater at 4, 8, 16, 20, and 28 inches from the measuring junction, corresponding to the positions in the thermocouple where the double-bore tubing was joined. Since no effects are noticeable at 12 and 24″, it is thought likely that the tubes were butted more tightly together at these positions. It is evident that short lengths of double-bore tubing offer poor protection.

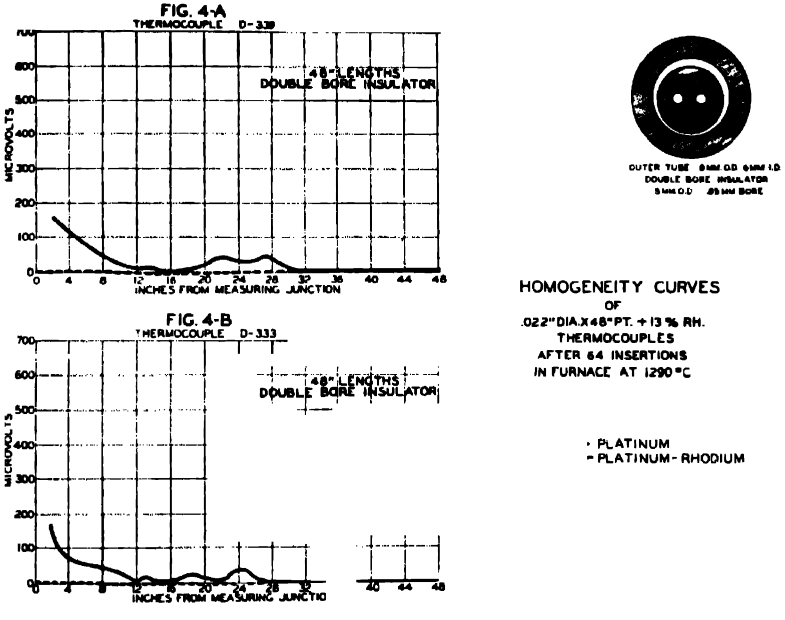
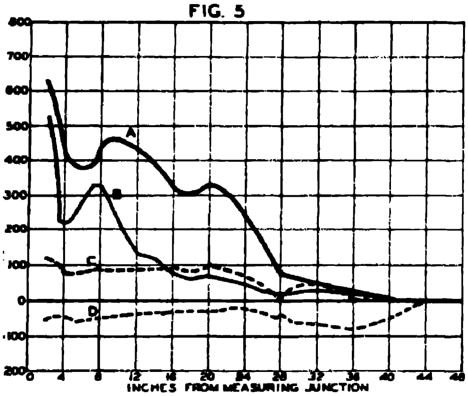


FIG. 4.

FIG. 5



HOMOGENEITY CURVES
OF THERMOCOUPLE D-328
WITH 4 INCH LENGTHS
OF DOUBLE BORE TUBING.

A- PT. C-PT.+RH.
AFTER 64 INSERTIONS IN FURNACE
PRIMARY TUBE 9MM. O.D., 6MM. I.D.

B- PT. D-PT.+RH.
AFTER 14 DAYS IN FURNACE
PRIMARY TUBE 19MM O.D., 14MM. I.D.

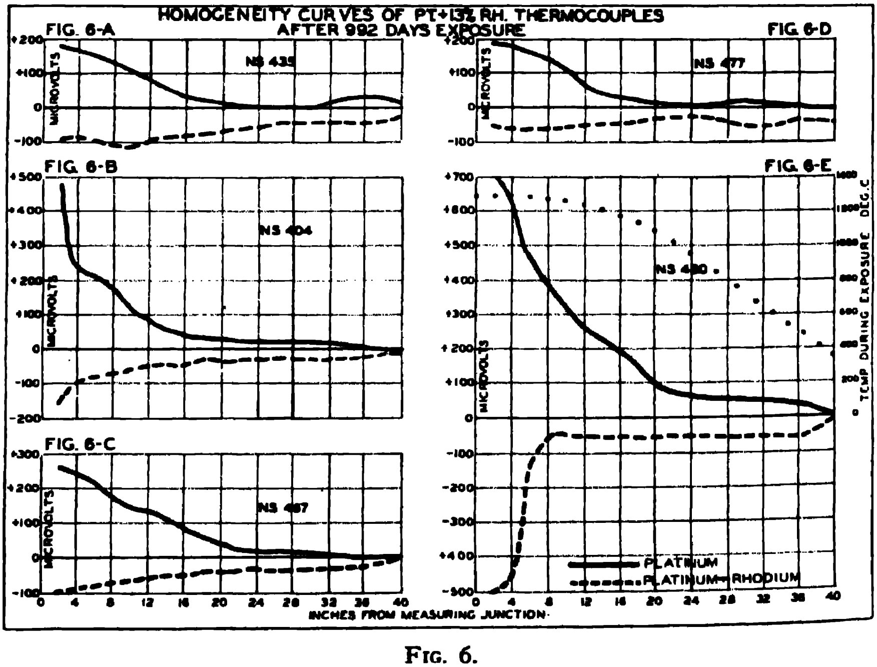


FIG. 6.

Fig. 2B is a curve for a thermocouple made up in a similar manner, except that 12″ lengths of double-bore tubing were used. Some improvement over the 4″ lengths is noticeable; however, the homogeneity curve is far from satisfactory.

Two thermocouples were mounted in what was intended to have been double protection as shown by the arrangements of the tubes in Fig. 3. The same size double-bore insulating tubing was used as in Fig. 2A, the only difference being an additional primary tube. Although better protection was no doubt obtained from the outside influences, contamination was such that the peak of the homogeneity curve has been moved back toward the colder end of the tube. Under certain conditions of immersion, this would cause large errors in the emf developed. Previous experience has led to the belief that the poor showing of this type of protection was due to inadequate breathing caused by the small air space between the double-bore tubing and the inner primary tube.

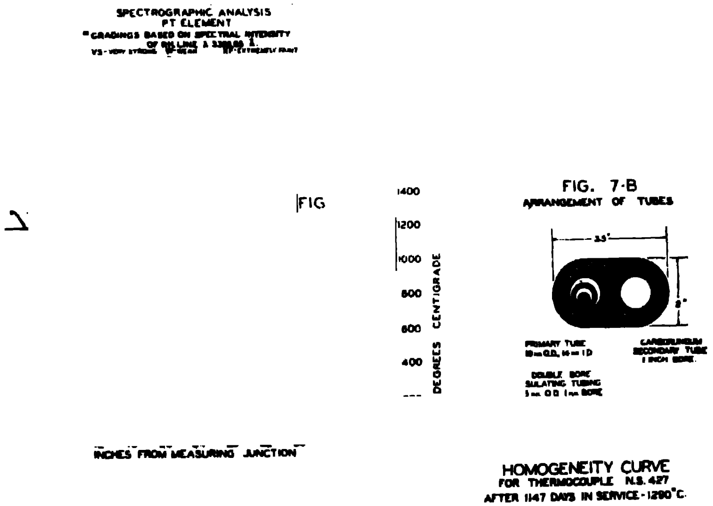


Fig. 7.

The best protection was obtained by using a single length of large diameter, double-bore tubing throughout the entire 48″ length of the thermocouple. This tube, on account of the larger diameter, acted in the same manner as a primary tube, except for the open end near the measuring junction. The thermocouples of Figs. 4A and 4B were made in the same manner, except that the primary tube of the couple represented in Fig. 4A had been given a special glazing treatment by the maker.

The small inhomogeneity around the 24″ section has been assumed to be caused by a concentration of silica in this part of the tube. It seems that the effect is more noticeable when the tube is new, and gradually decreases after a week or two of exposure. Such a condition in the primary tube would account for the thermocouples of Figs. 3A and 3B, which were exposed with double primary tubes, having been contaminated to a greater extent in the center than at the junction of the elements where the wires were exposed. That some of the contamination is removed when the tube is allowed to breathe is evident from further tests made on the thermocouple of Fig. 2A, which had been insulated with 4" lengths of double-bore tubing. After the homogeneity test was made, this thermocouple was transferred to a larger diameter primary tube and put into a furnace. After 14 days the inhomogeneities diminished to about one-half, as is shown in Fig. 5. Curves A and C are the same as those in Fig. 2A, and Curves B and D were obtained after the thermocouple was exposed in the larger primary tube for 14 days.

It should be understood that in these tests conditions were such that deterioration was accelerated. The tubes were smaller than are usually used, the platinum had been given a short electrical anneal and the thermocouples were moved about quite frequently during exposure.

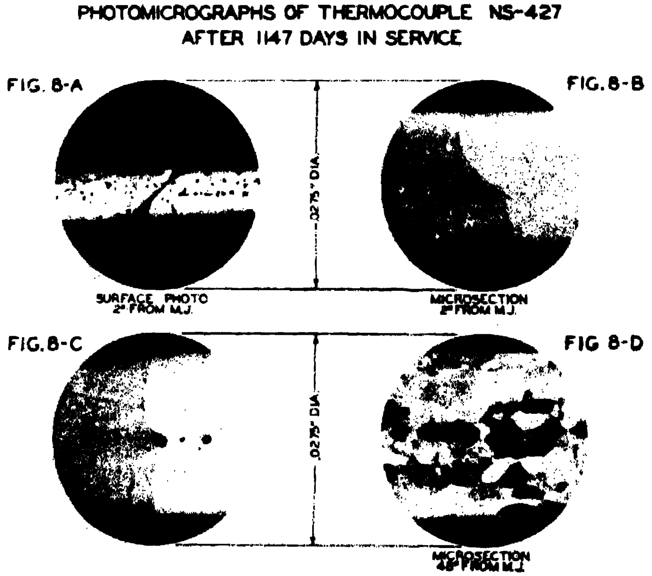

PHOTOMICROGRAPHS OF THERMOCOUPLE NS-427
AFTER 1147 DAYS IN SERVICE

FIG. 8-A
FIG. 8-B
.0275" DIA.
SURFACE PHOTO 2" FROM M.J.
MICROSECTION 2" FROM M.J.
FIG. 8-C
FIG 8-D
.0275" DIA.
MICROSECTION 48" FROM M.J.

FIG. 8.

In order to substantiate the results of these tests in a commercial installation, six thermocouples were made with single lengths of double-bore tubing and primary tubes of 14 mm I. D. Each thermocouple was put into one well of a double-bore Carborundum secondary protection tube mounted in the furnace. The life of all six of these thermocouples was over twice that usually obtained in these positions. They were not disturbed during their entire life. Checking was done in the usual manner of inserting a standard thermocouple in the vacant well of the secondary tube. They were finally removed from service because of a furnace shutdown. Prior to removal, the emfs were checked and found to be within 6 to 9° of the standard 13 per cent rhodium table.

Fig. 6 shows the homogeneity curves obtained from five of these thermocouples after they had been removed from service. The fact that their life was considerably longer than usual is probably due to the fact that very little change occurred throughout the portion of the tube having the largest temperature gradient.

The curve for the sixth thermocouple of this group is shown in Fig. 7A. Spectrographic analyses taken at various places show the chemical changes which took place during the time it was in service. The analysis at 48" (cold end) is with the exception of the questionable presence of rhodium identical with that obtained on the wire when it was new. It is interesting to note that traces of silver and palladium have disappeared in the end of the platinum-rhodium element which had been in the hot zone. Those of copper and iron have been diminished, but that of silicon has been increased. In the platinum element there was a gain of iron and a loss of copper. While the figures for the rhodium content of the platinum element are arbitrary values, they do indicate a greater amount near the measuring junction and a gradual decrease towards the cold end. Assuming that the inhomogeneity of the thermocouple was caused entirely by a transfer of rhodium, at 4" from the measuring junction, the rhodium contents were calculated to be 0.16 per cent for the platinum element and 12.7 per cent for the other.

Photomicrographs of the platinum element show that the grain size, which averaged about 0.002" at the cold end, had been increased to the full diameter of the wire (0.022") throughout the greater portion toward the measuring junction.

Figs. 8B and 8C are representative of the grain structure of the platinum element from the measuring junction to about 36" away. Fig. 8A shows a surface photograph of a large grain boundary such as appeared at several places in the first 3 inches from the measuring junction. Throughout the remainder of the element there were no noticeable broad grain boundaries. It seems that the absences of broad grain boundaries throughout the greater portion of this thermoelement contributed to the slow rate of contamination.

It should be pointed out that these tests were made under what might be considered ideal conditions of immersion. The temperature gradient was uniform and relatively small in all portions of the tubes. Quite different homogeneity curves would be expected for different conditions of immersion. In installations, where sharp gradients occur in the tube, the life of the thermocouple would be reduced as the errors due to inhomogeneity would be much larger.

Conclusions

In conclusion it has been found that better accuracy and longer life can be expected with platinum thermocouples if the following considerations are observed:

(1) A single length of double-bore insulating tubing should be used throughout the entire length of the thermoelements.

(2) Ample air space should be provided between the double-bore tubing and the primary tube to allow sufficient breathing.

(3) Thermocouples should be disturbed as little as possible after being put into service and their mounting should provide for a uniform movement of the wires from expansion and contraction.

Observance of these factors has led to doubling the life of test thermocouples in a commercial installation and a general increase in the life of all working thermocouples.

Acknowledgment

The author wishes to acknowledge the coöperation and assistance of Dr. Bert Brenner of Sigmund Cohn, and of various associates in the Research Division of The New Jersey Zinc Company in preparing this paper.

Discussion

H. E. Stauss, Baker & Co.: The results given in this paper are extremely important because they represent the practical experience of a large commercial user of platinum-rhodium thermocouples. They show that a large grain size accelerates the destruction of a couple and that intermittent removal of a couple for calibration shortens its life. These facts suggest that failure is frequently the result of offsetting of large crystals, a phenomenon like that observed in tungsten lamps, and that failure is often mechanical in origin and not the result of contamination. The slight flexures and distortions produced in the wires by moving a thermocouple for calibration would supply the stresses that produce offsetting and at the same time create a slight amount of work-hardening which would induce, on subsequent heating, an enhanced grain size to give rise to accelerated offsetting. The increase in life of permanently installed couples, as compared with those removed for frequent calibration, can, therefore, be explained on purely metallurgical grounds. Homewood appears to be the first to have considered this important phenomenon with thermocouples.

The paper shows that contamination occurs in the wires of a thermocouple between the lengths of insulating tubing. This, of course, is where the wire is exposed and unprotected by the insulating tubes. However, one wonders if the strains produced in these unprotected regions may encourage diffusion as well as grain growth, inasmuch as diffusion in a metal appears to be accelerated by work-hardening preceding a heat treatment. It is just possible that the practice of not moving thermocouples may retard chemical contamination as well as mechanical failure.

The high quality of platinum-rhodium thermocouples available commercially today makes it entirely practical, with couples used for ordinary commercial temperature measurements (as distinguished from precision measurements), to dispense entirely with any thermal treatment for conditioning and to install them directly as received from the manufacturer in the hard-worked or unannealed state. This practice would have two advantages in the light of Homewood's results. First, any strains imparted during installation would be negligible additions to the large strains already present and would have no appreciable influence on later recrystallization. Similar strains impressed on soft wire might well give rise to an exaggerated grain size. Secondly, it would avoid coarse recrystallization attendant upon heating the wires at a temperature higher than those encountered in service. It is well known that the size of crystals produced in a metal is a function of both the temperature and the time of annealing, and increases with both. Consequently the high temperature of a preliminary conditioning or stabilization is an important factor in the production of large crystals.

R. B. Sosman, Research Laboratory, United States Steel Corporation: Are the alkali or alkaline-earth metals included in the spectrographic analysis? I am thinking of the possibility of contamination of the wire from the protecting porcelain tube, which usually contains some feldspar (sodium-potassium-calcium alumo-silicate). It is known that platinum takes up a little calcium if melted in a lime crucible, and that it acts as a strong reducing agent toward the oxides of iron.

C. F. Homewood: No. Qualitative determinations were made on a large Littrow type spectrograph between wave-lengths 3400 and 2300A, and faint traces of the alkaline metals would not be detected in this range.

Changes in Platinum Thermocouples Due to Oxidation

BERT BRENNER
Sigmund Cohn, New York City

If platinum thermocouples are left in service over a long period of time, a black discoloration appears on that part of the platinum-rhodium leg that is in the temperature range 400-600 °C. The discoloration is caused by the formation of rhodium oxide. The length of the discolored zone varies with the length of time the couple has been exposed and with the temperature gradient along the wire. If the couple is not disturbed, the length of the discolored zone will reach a maximum value which will be reasonably constant for long periods.

The oxidation of some of the rhodium changes the effective composition of the alloy in that region. Since there is a difference in temperature between the two ends of the zone, the emf of the couple is changed. An illustration can be taken from Fig. 7A of the paper "Factors Affecting the Life of Platinum Thermocouples" in this Symposium by C. F. Homewood. Observations on a platinum-platinum 13 per cent rhodium couple which had been in service more than three years at 1290 °C revealed that the oxidized portion of the platinum rhodium leg was about 12″ long, extending to about 6″ from the cold junction, and that the emf at 1290 °C at the initial immersion had decreased by the equivalent of 6 to 9 °C. The portion of the wires where loss of rhodium through volatilization from the platinum rhodium leg occurred, with consequent contamination of the platinum leg, had been in a region of rather uniformly higher temperature.

It would seem to be a conservative estimate that the inhomogeneity through the oxidized zone of the platinum-rhodium leg would affect the final calibration to the extent of minus 3 to minus 4 °C. Errors arising from this source may, therefore, be significant, depending upon the desired accuracy of the measurements.

It should be stated, however, that a platinum-platinum-rhodium thermocouple which changes only 6 to 9° in over three years of continuous service at 1290 °C must be considered to have rendered an excellent performance.

Messrs. Wensel and Roeser, at the National Bureau of Standards, have also observed the oxidation of platinum-rhodium wire. They heated the wires electrically, in air, at about 800 °C, for 35 days. At the end of that time the emf of the 10-per cent alloy versus platinum at 1200° had decreased 26 microvolts, and that of the 13-per cent alloy 29 microvolts. When the wires were then heated briefly at 1450°, the emfs at 1200° were restored to within 4 and 6 microvolts respectively. These changes occurred because the rhodium oxide was dissociated at the higher temperature and the original compositions were substantially restored.

Mr. Homewood has clearly demonstrated the beneficial effect on the useful life of platinum-platinum rhodium thermocouples of full-length inner protecting tubes, and of outer protecting tubes which are large enough to permit "breathing," thereby maintaining an oxidizing atmosphere around the couples.

Since 1935 the stability of the pure platinum leg of the couple has been increased by the practice of annealing the wire at a low temperature. It was found that chemically pure platinum wire can be completely annealed at 400 °C in one hour. Wire annealed slowly at this temperature *in air* (by heating it in a platinum dish in a furnace, not by resistance heating) shows an improved behavior with respect to contamination in subsequent service as compared to wire annealed (by electrical heating) at 1450 °C. Under a given set of severe conditions, the latter wire might be contaminated so badly as to become positive to uncontaminated wire (at 1200°) by some 1300 microvolts, whereas the former wire would show no greater change than 60 microvolts. This chemical or catalytical inertness seems to necessitate the assumption of an activated adsorbed or chemisorbed layer of oxygen on the pure platinum wire at the lower annealing temperature. For example, there is a distinct difference in the appearance of the surface of the two types of wire, that annealed at high temperatures displaying wide grain boundaries and pits, caused probably by the escape of oxygen absorbed by the metal during melting.

Some Observations on Chemically Pure Platinum Wire for Resistance Thermometers

Resistivity measurements of C.P. platinum wire (diameter .0015") showed a variation in different parts along the length of a wire of plus or minus .25 per cent, which is thought to be caused by a variable oxygen content taken up by the platinum during melting, for when an ingot of metal of this kind is heated to incipient melting but not melted, the non-uniformity in resistance decreases to plus or minus .04 per cent.

The oxygen content of a given length of wire heated in air does not change if the wire is not overheated; it is affected, however, by heating in vacuum at relatively low temperatures. The calibration and performance of a number of resistance thermometers indicate that the oxygen does not noticeably affect the temperature coefficient of resistance of sufficiently pure platinum.

Acknowledgment

I wish to thank Messrs. C. F. Homewood and A. O. Ashman of the New Jersey Zinc Company, and H. T. Wensel and W. F. Roeser of the National Bureau of Standards for their valued assistance.

Discussion

E. Wichers, National Bureau of Standards: With regard to varying practice in the so-called annealing of thermocouples prior to calibration, a distinction should be made between true annealing and another effect of prolonged heating (in air) on the thermal emf of the couple. If either element of the couple contains small proportions of base-metal impurities such as iron, or more particularly calcium, zirconium, or thorium derived from the refractories in which the metal has been melted, heating in air at high temperatures will cause a decrease in the thermal emf of the wire which is presumably caused by the conversion of these impurities to their oxides. This effect was demonstrated with respect to calcium at the National Bureau of Standards many years ago. Platinum wire contaminated with calcium will gradually change in thermal emf, when heated in air at a high temperature, until it becomes virtually neutral to pure platinum.

If the metals used in the couple are thus contaminated, the emf of the couple will gradually change in service, because of the slow oxidation of the impurities, unless the couple has been stabilized by prolonged heat treatment prior to calibration. The practice of prolonged "annealing" at high temperature probably arose from the observation of changes of this kind in the emf of couples. However, this effect of heating should not be confused with annealing, and the practice might well be unnecessary if the metals can be prepared in sufficiently pure condition.

Reply

The author fully agrees with Dr. Wichers' comments. Annealing, *i.e.*, recrystallization, seems necessary to remove any possible strain which might affect the thermoelectric properties of even the purest platinum wire.

Some years ago the author published data on what he then considered good manufacturing practice for platinum and platinum-rhodium thermocouple wires.[1] High-temperature treatment by resistance annealing of the welded couples to "stabilize" them then was found detrimental to optimum performance and life. Highest-purity platinum wire does not require high-temperature "stabilization," nor annealing at 400 °C after it leaves the manufacturer. An exception is made for calibration and standardizing purposes in order to ascertain and severely test the quality of the wire; in this case extreme treatment seems advisable. However, wire so treated should be regarded as "standard" and not be subjected to ordinary use.

The author recommends a low-temperature anneal only for C.P. platinum wire to be used for the platinum leg of platinum-platinum rhodium thermocouples. C.P. platinum wire of a purity of plus or minus 5 microvolts versus "Pt 27," after a cold reduction of about 90 per cent, recrystallizes at 400 °C in one hour and shows an elongation of 38 per cent in 2 inches. There can be no doubt that this wire is annealed. Platinum 10 per cent or 13 per cent rhodium wire certainly would not recrystallize at this temperature.

It is not believed that an increased grain growth at high temperatures would affect the rate of diffusion and contamination to as great an extent as the migration of oxygen (originally dissolved in the molten platinum) into the grain boundaries, and the pitting that results from its release.

The assumption of an activated adsorbed or chemisorbed layer of oxygen (not platinum oxides) on the surface of platinum wire, furnace-annealed in air at low temperatures, would seem to explain satisfactorily its improved performance and longer life in service.

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The Silver-Constantan Plated Thermopile

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AND

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A multi-junction thermopile may be employed to measure energy interchanges, and is commonly used to measure irradiation. A radiation thermopile of the soldered junction type is difficult and costly to construct, and for a given thermoelectric effect the sensitivity limit is soon reached because of the difficulty of crowding more and more junctions into a given space.

Another type of construction was first proposed and used by Wilson and Epps[1] (who considered many of the problems in building thermocouples by electrodeposition). Jones[2] later applied this method to developing a rapid-response thermopile. This paper will describe a thermopile designed for use as a radiometer.[3] The thermopile is of the electrodeposition type and is similar to those previously proposed, but possesses additional constructional features.

The sensitive element was developed for use in connection with the research program of the Orchard Heating Investigation of the Division of Agricultural Engineering, University of California. An instrument for measuring the rate of radiant energy transfer from orchard heaters as a function of horizontal and vertical angles was desired. A non-selective thermopile was decided upon.

Theory

The energy conversion principle supplies the basis for using a thermopile as a radiation metering instrument. The response with respect to energy rate per unit area falling upon the receiving element of the thermopile is approximately linear.

A heat balance on the thermopile subject to certain simplifications indicates that the rate of energy absorption per unit area $= f(t_h - t_s) + \frac{k}{L}(t_h - t_c) = ft_h + \frac{k}{L}t_h - ft_s - \frac{k}{L}t_c = C_1t_h + C_2$, where C_1 and C_2 are constants and

f = conductance per unit area for convection and radiation for small differences between t_h and t_s;
t_h = temperature of the irradiated junctions;
t_s = temperature of surroundings, assumed constant over duration of calibration;
k = thermal conductivity of the wires;
L = length of wires under consideration;
t_c = temperature of the shielded junctions, assumed to be constant over duration of calibration.

Therefore, the rate of energy absorption is a linear function of t_h.

The emf generated by a thermocouple is approximately linear with respect to temperature difference of the order of 1 °C ($\cong$2 °F).

Then $G = A + Bv$,
where G = irradiation of the receiver per unit area;
A = a constant for a given energy level of the surroundings;
B = a constant (reciprocal of the sensitivity);
v = emf generated by the thermopile.

The curve illustrated in Fig. 1 may be drawn if calibrating devices (surface or hohlraum) are available.

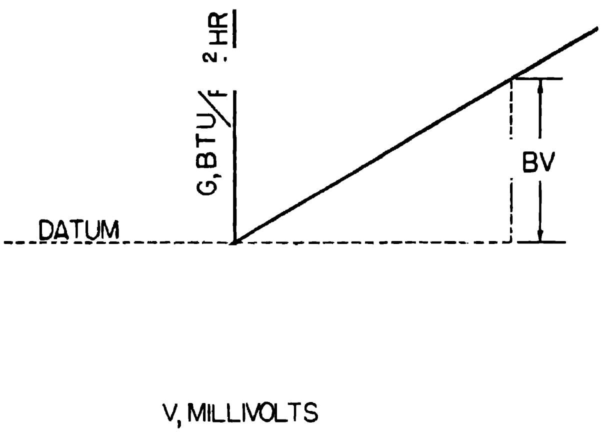
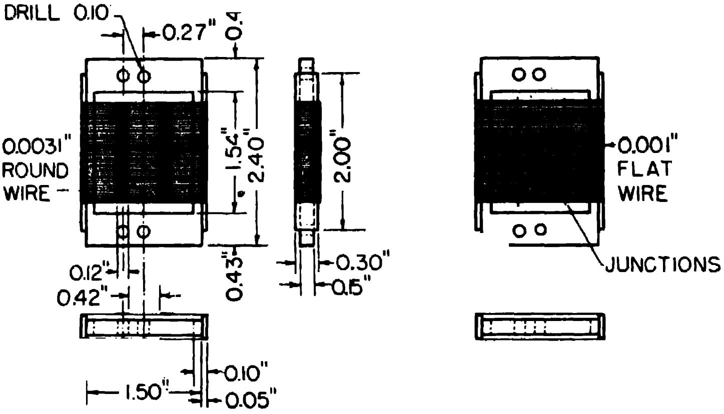


Fig. 1. Typical calibration curve.

Design and Construction

The thermopile consists of many turns of fine constantan wire wound over glass insulators which are fastened to a heavy copper spool. Silver is deposited on a portion of the coil of wire by electrodeposition. The electrolyte level forms a line of silver-constantan junctions. Two lines of junctions (hot and cold) are formed on one face of the coil by electroplating in several stages. Wilson and Epps[4] have shown that, since the electrical conductivity of the constantan is much lower than that of the silver, the shunting effect of the constantan core is negligible.

Two types of thermopiles were developed which will be referred to as element A and element B. Details of elements A and B are shown in Fig. 2. Element A is designed for high sensitivity and stability. Rapidity of response is a secondary consideration. The No. 40 A.W.G. constantan wire is wound on a copper frame over insulators consisting of glass strips. The wire is plated with silver so that both junctions are on the front and are ½ inch apart, which is the optimum distance.[5] Tinfoil strips, blackened on the exposed side, are fastened to the two lines of junctions by means of dilute shellac. The cold junction strip (receiver) is shielded; the hot junction (receiver) is exposed to radiant energy from the source by a narrow window. Moll[6] obtains stability by placing the "passive" junctions in semi-direct contact with a heavy copper base of high heat capacity; the "active" junctions are spaced away from the heavy base to minimize their heat capacity. By virtue of its construction a much simpler method is



ELEMENT A ELEMENT B

FIG. 2. Details of sensitive elements.

obtained with the wound thermopile in positioning the "passive" junctions so as to receive radiant energy from a blackened baffle and the inner surface of a heavy metal housing. The opening in the spool located below both the "active" and "passive" junctions minimizes the heat capacity of the "active" junction system and maintains both junctions in the same environmental conditions when no radiant energy is directed into the instrument. A stable zero, high sensitivity and reasonably rapid response are obtained. Element A is wound 104 junctions to the inch by means of a specially built coil winder and is composed of approximately 160 junctions. Its reciprocal sensitivity is found to be 0 :038 gm cal/cm^2 min mv (6.78 Btu/ft^2 hr mv). The time of response and recovery to zero, with energy rates of the order of 0.317 gm cal/cm^2 min (70 Btu/ft^2 hr) was found to be approximately 40 seconds. Fig. 3 is a photograph of element A.

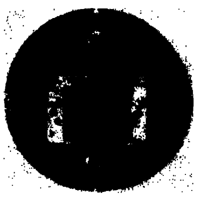


FIG. 3. Photograph of element A.

The tinfoil receiver increases the response time, but when the irradiation is not fluctuating rapidly, the gain in sensitivity justifies its use. However, if rapid response is required, element B may be desirable. The No. 40 A.W.G. constantan wire is rolled into ribbon to a thickness of approximately 0.001 inch; the spool is wound and plated in the same manner as is element A, but the tinfoil receivers are not placed over the hot and cold junctions. Applying the blacking directly to the junctions makes the heat capacity of the hot junction of element B much less than element A, resulting in a much more rapid response for the former. Maximum galvanometer deflection was reached in appoximately 10 seconds when the exposed receiver of element B was irradiated. More rapid response could be obtained by using finer wire. Element B is wound on the same type of spool as is utilized for element A and the same conditions of stability are realized. The sensitivity of element B is limited by the number of turns which may be wound with a given width of ribbon (approximately 45 turns per inch for a ribbon width of 0.001 inch).

FIG. 4.
Photograph of Plating Equipment.

Electroplating is accomplished in three separate operations. Fig. 4 reveals the plating equipment showing an element arranged for plating. The element is mounted on a Bakelite support held in place by rubber bands which also maintain a thin metal strip in electrical contact with each individual turn. The level of the electrolyte determines the line of junctions. The second operation establishes the second line of junctions $\frac{1}{2}$ inch from the first line. The element is completed by plating the entire back.

The electrolyte solution is:

Potassium cyanide	30.0 grams
Silver chloride	16.6 grams
Distilled water to make	500 cc

A hot potassium cyanide solution is used to clean the coils before plating. The current is maintained at 0.04 ampere in the first two operations and the time of plating is 45 minutes, making the cross-sectional area of the silver approximately 35 per cent of the constantan.[7] The current is maintained at 0.025 ampere when plating on the back, and the time of plating is 6 hours. Increasing the plating on the back decreases the overall thermopile resistance which has an optimum value when the resistance of the constantan path equals that of the silver path. The overall resistance of element A is 280 ohms.

Calibration

For the purpose of maintaining stability and calibration, the element is mounted in a heavy metal case. Fig. 5 presents an assembly drawing of the unit showing the thermopile element (T) rigidly mounted on a saddle. Details of the housing and methods of calibration are available.[8]

Conclusions

The construction of the silver-constantan plated radiation thermopile is relatively simple. It is rugged, of medium sensitivity and of fairly quick response. By a proper choice of calibrating devices, it may be used to measure radiant energy interchanges for any system if the energy rate is within the sensitivity range of the instrument. The performance of the thermopile compares favorably with that of commercial thermopiles; the sensitivity of a typical unit is 1 millivolt for $\frac{0.038 \text{ gm cal}}{\text{cm}^2 \text{ min}}$, or 6.8 Btu/ft^2 hr. One commercial thermopile available possesses a slightly greater sensitivity, but it is more costly and more difficult to construct.

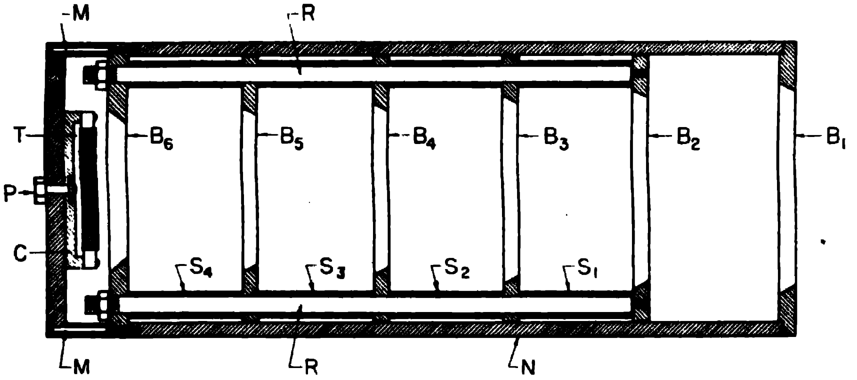


FIG. 5. Thermopile radiometer assembly.

Acknowledgments

The authors are deeply indebted to the late Dr. V. H. Cherry who conducted most of the research and developed a large portion of the experimental and constructional technic. Also, the contributions of F. A. Brooks, Professor of Agricultural Engineering at the University of California and member of the Orchard Heating Investigation Staff; F. Lory and H. W. Sylvis, members of the laboratory staff; D. F. Owens, former graduate student at the University of California, Berkeley; and F. A. Ryder, Staff, Testing Agency of the Department of Motor Vehicles, University of California, Berkeley, are gratefully acknowledged. Construction assistance was had under W.P.A. Project No. 465-03-0-628.

Discussion

F. A. Brooks, University of California: The primary limitation of the design was that it be usable in the field with a Leeds & Northrup semi-precision potentiometer (Model 8662). "Ruggedness" for this purpose meant the ability to withstand transportation in a light truck across plowed field furrows. The machine-wound plated wire element of large number of turns was completely successful in this regard. The large number of parallel wires creates an optical illusion of apparently small receiver area per couple. Actually this unit area of 0.78 mm^2 per couple is larger than that of many conventional thermopiles.

The net nocturnal atmospheric radiation flux density to be measured with the above potentiometer (used for other thermocouple observations of field temperatures) has a maximum average intensity toward the zenith of about 0.036 cal/cm^2 min steradian (8 B.t.u./ft^2 hr steradian). This is so weak that the design objective in the radiometer element was to obtain maximum emf to favor the potentiometer. The limitation in this objective was the minimum observable null-point galvanometer deflection which was about 0.003 mv when outdoors at night in freezing weather. When in the field house readings to 1 microvolt were customary. The zenith net radiation gave approximately 0.3 millivolts. The net atmospheric radiation exchange goes to zero near the horizon.

If this thermopile were to be used primarily with a deflection galvanometer, the design criteria would be different in that one would consider the relation between thermopile resistance and galvanometer coil resistance which for optimum response depends upon the apportionment of heat transfer between the receiver surface itself and the thermocouple wires. The size of receiver area again depends upon the power wanted to operate the deflection instrument, but the number of couples for a fixed receiver area would be less than in the above example if maximum galvanometer deflection is desired. This criterion for a given galvanometer coil is that

$$n = \sqrt{\frac{1}{AB}}$$

where n = optimum number of couples

$$A = \frac{\text{heat transfer rate via 1 pair of wires}}{\text{heat transfer rate from receiver alone}}$$

$$B = \frac{\text{thermopile resistance per couple}}{\text{resistance of the galvanometer coil}}$$

The physical meaning of this deflection design criterion is that the ratio of the rate of heat transfer from the receiver alone to that via the wires, be equal to the ratio of the resistance of the thermopile to that of the galvanometer coil; assuming the critical resistance is of such value that the galvanometer operation is satisfactory. Although the above criterion is specific it is not sharply selective, so there is considerable latitude in choosing the number of couples to suit a given receiver area.

If the galvanometer coil could be selected to suit the radiometer, the best response would be obtained if the coil resistance were equal to the thermopile resistance. This 1:1 ratio indicates that optimum thermopile design calls for as many couples per given receiver as will provide the same amount of heat transfer via the wires as from the receiver itself. This criterion applied to the element under discussion would call for much fewer turns per inch, but this would lessen the ruggedness of the element.

The radiometer element described was also used extensively with a microammeter of 280 ohms in measuring the radiant energy output of orchard heaters. Had the number of couples been selected to suit this deflection instrument, a gain in response of about 25% could have been obtained.

The analytical derivation of the criterion for optimum number of couples for given receiver area to obtain maximum deflection with a given galvanometer coil is as follows:

The temperature difference between the receiver strip and its surroundings is

$$\Delta t = \frac{E}{f_R + f_N}$$

$$\frac{E}{f_R + nAf_R}$$

The thermopile emf

$$e_N = ne_o\,\Delta t = \frac{ne_oE}{f_R + nAf_R}$$

$$= \frac{ne_oE}{f_R(1 + nA)}$$

The galvanometer current

$$I = \frac{e_N}{R_G + R_N}$$

$$\frac{e_N}{R_G + nBR_G}$$

$$\frac{\dfrac{ne_oE}{f_R(1 + nA)}}{R_G(1 + nB)}$$

$$= \frac{e_oE}{f_RR_G}\left(\frac{n}{(1 + nA)(1 + nB)}\right)$$

$$= C\left\{\frac{1}{\dfrac{1 + n(A + B) + n^2AB}{n}}\right.$$

where Δt, [°F], = temperature excess of receiver

E, $\left[\frac{\text{Btu}}{\text{hr}}\right]$, = energy input to receiver

f_R, $\left[\frac{\text{Btu/hr}}{{}^\circ\text{F}}\right]$, = over-all heat transfer factor of receiver

f_N, $\left[\frac{\text{Btu/hr}}{{}^\circ\text{F}}\right]$, = over-all heat transfer factor via couple wires

n, [--], = number of pairs of thermocouple wires

A, [--], = ratio $\dfrac{\text{heat transfer rate via 1 pr wires}}{\text{heat transfer rate from receiver alone}}$

i.e., $\frac{1}{nA}$ = criterion heat transfer ratio

e_N, [volts], = emf of thermopile

e_o, $\left[\frac{\text{volt}}{{}^\circ\text{F}}\right]$, = emf/°F of single thermocouple

I, [ampere], = current in the galvanometer circuit

R_G, [ohm], = resistance of galvanometer coil

R_N, [ohm], = resistance of thermopile

B, [--], = ratio $\dfrac{\text{resistance per couple}}{\text{resistance of galv. coil}}$

i.e., nB = criterion resistance ratio

C, $\frac{\text{volt}}{\text{ohm}}$, = receiver-galvanometer constant

This current will be a maximum if $\left(\frac{1}{n} + (A + B) + nAB\right)$ is a minimum.

The derivative of this expression relative to n is $-\frac{1}{n^2} + 0 + AB$, and set equal to zero yields the result $\frac{1}{n^2} = AB$ or $\frac{1}{nA} = nB$ for maximum galvanometer current. This is the design criterion mentioned above to choose the optimum number of couples for a given receiver strip and given galvanometer coil.

F. S. Brackett, U. S. Public Health Service: I have been asked to comment on the article of Gier and Boelter entitled "The Silver-Constantan Plated Thermopile." I do so with some hesitation in view of the fact that I recognize that this thermopile has certainly served a useful purpose for the authors and therefore may be of value to others with a similar problem. Nevertheless, viewed from the standpoint of a contribution to the knowledge of radiometry, a rather critical point of view may be taken.

The designation of the voltage produced by a given flux, or flux density as the case may be, while a useful calibration constant, is not in any sense a factor of merit, and does not furnish the basis for judging the value of such an instrument. The question immediately arises as to how accurately such voltage can be measured, and in turn, the minimum voltage increase which can be observed. Although it is the voltage which is measured with a potentiometer, the balancing of the potentiometer necessarily involves the use of a current-measuring device. Hence the current produced is an essential consideration. In a general way the critical damping resistance of the galvanometer must be matched to the thermopile, so that some consideration of its characteristics is necessarily involved. The limitation on the minimum measurable potential difference produced, and hence the accuracy of observation, is chiefly a matter of residual fluctuation in current, as well as the drift which arises in use.

As an illustration, this 104-junction thermopile produces .375 volt per watt per cm^2 of flux density, yet the current corresponding is approximately .0012 ampere per watt per cm^2 of flux density (assuming a 40-ohm galvanometer with suitable critical damping resistance), whereas a 12-junction thermopile which recently came to my attention produced .067 volt per watt per cm^2, which corresponded to .0028 ampere per watt per cm^2, using a suitable galvanometer. Since, however, the galvanometer with the higher critical damping resistance which may be used with a 104-junction pile has approximately twice the sensitivity, the two piles are of about equivalent value, other things being equal.

As a further illustration, a single-vacuum thermocouple may produce .12 volt per watt per cm^2, with a corresponding current, per watt per cm^2, of .003 ampere.

As will be immediately seen from these illustrations, little is gained by the increase in the number of junctions except as they prove to be a convenience in attaining suitable area of surface or ease of mechanical construction. So far in the discussion we have assumed that the problem is to measure flux density rather than to measure incident radiant power, that is, one is not limited as to the area which is utilizable for the receivers. Many problems in radiometry require that an extremely small amount of radiant power be detected, ragardless of the size of the receiver. Thus, in the case of spectral radiometry by suitable optical means, the total power output may be concentrated on the receiver of a square millimeter or less area. The merit of the junction arises from its ability to detect an extremely small amount of radiant power rather than radiant flux density. With such a single junction, less than one-thousandth of an erg per second may be detected. For such purposes these relatively gross and satisfactory rugged piles are at a serious disadvantage. Furthermore, by utilizing very small junctions of extremely low heat capacity, times of response are greatly diminished. As against the 10-second time indicated for the 104-junction pile, one-tenth to one-quarter of a second period is attained.

It has been by observation that a pile is only as good as a single junction or a few junctions, provided the optimum relationships of constants can be attained for each junction. Thus, if multiplicity is gained at the sacrifice of favorable selection of thermal elements, *i.e.*, silver constantan as against Chromel-P-constantan or bismuth bismuth-tin, the resulting instrument is just that much inferior to one constructed in accordance with optimal demands, and with a lesser number of junctions. For an atmospheric pressure pile where the optimal heat exchange is attained with low resistance and the area is more or less unlimited, some 4 to 20 junctions may prove advantageous. If on the other hand, a minimum total flux must be measured, the advantages are all in favor of a single junction which can be more adequately housed in the controlling hohlraun. Furthermore, extreme lightness such as is attainable in such rugged materials as Chromel-P constantan make for greater speed of response and ease of use.

The optimal relations of area of receiver to length of lead, electrical resistance and heat conductivity, which have been treated at great length in other papers, are just as pertinent in the construction of thermopiles as single junctions and should be given full consideration.

In conclusion I would suggest that thermopiles constructed for measuring flux density be judged on the basis of the smallest increment of flux density which may be measured with certainty, and that thermo-junctions or thermopiles designed to measure total flux be judged by the smallest increment of total flux which can be measured with certainty. Clear statements as to fluctuation and drift are of special value in connection with any such description of technic.

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Appendix

The tables of data in this appendix were prepared by Wm. F. Roeser and H. T. Wensel of the Pyrometry Section of the National Bureau of Standards.

During the past twenty years, measurements in that Section have resulted in the accumulation of a considerable amount of data on the spectral emissivities, thermoelectric properties and resistance-temperature relations of metals and alloys. These data have all been included and, in many instances, are published here for the first time. All of Tables 11, 13 and 15 fall into this class. Credit for such data is due principally to Wm. F. Roeser.

The data in Table 14, with the exception of those for the copper-nickel alloys, have been taken from the "International Critical Tables." The data in the other tables were obtained from the above-mentioned as well as from other sources. In some cases where it was felt that the omission of data which were not available would be unfortunate, measurements were made to obtain such data. Credit for this work is due to A. I. Dahl of the Pyrometry Section of the National Bureau of Standards.

Some of the tables obviously are simply the result of computation.

Table 1. Reference Table for Pt to Pt – 10 Per Cent Rh Thermocouple.

(Emfs are expressed in microvolts and temperatures in °C. Cold junctions at 0 °C.)

E (μv)	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	E (μv)
0	0	146.9	265.0	373.7	477.7	578.1	675.3	769.5	861.0	0
	17.7	*12.5*	*11.2*	*10.5*	*10.2*	*9.9*	*9.5*	*9.3*	*9.0*	
100	17.7	159.4	276.2	384.2	487.9	588.0	684.8	778.8	870.0	100
	16.7	*12.3*	*11.1*	*10.5*	*10.2*	*9.8*	*9.5*	*9.2*	*9.0*	
200	34.4	171.7	287.3	394.7	498.1	597.8	694.3	788.0	879.0	200
	15.8	*12.1*	*11.0*	*10.5*	*10.1*	*9.8*	*9.5*	*9.2*	*9.0*	
300	50.2	183.8	298.3	405.2	508.2	607.6	703.8	797.2	888.0	300
	15.2	*12.0*	*11.0*	*10.5*	*10.1*	*9.8*	*9.5*	*9.2*	*9.0*	
400	65.4	195.8	309.3	415.7	518.3	617.4	713.3	806.4	897.0	400
	14.6	*11.8*	*10.9*	*10.4*	*10.1*	*9.7*	*9.4*	*9.2*	*8.9*	
500	80.0	207.6	320.2	426.1	528.4	627.1	722.7	815.6	905.9	500
	14.1	*11.7*	*10.8*	*10.4*	*10.0*	*9.7*	*9.4*	*9.1*	*8.9*	
600	94.1	219.3	331.0	436.5	538.4	636.8	732.1	824.7	914.8	600
	13.7	*11.6*	*10.7*	*10.3*	*10.0*	*9.7*	*9.4*	*9.1*	*8.9*	
700	107.8	230.9	341.7	446.8	548.4	646.5	741.5	833.8	923.7	700
	13.3	*11.5*	*10.7*	*10.3*	*9.9*	*9.6*	*9.4*	*9.1*	*8.9*	
800	121.1	242.4	352.4	457.1	558.3	656.1	750.9	842.9	932.6	800
	13.0	*11.3*	*10.7*	*10.3*	*9.9*	*9.6*	*9.3*	*9.1*	*8.8*	
900	134.1	253.7	363.1	467.4	568.2	665.7	760.2	852.0	941.4	900
	12.8	*11.3*	*10.6*	*10.3*	*9.9*	*9.6*	*9.3*	*9.0*	*8.8*	
1,000	146.9	265.0	373.7	477.7	578.1	675.3	769.5	861.0	950.2	1,000

E (μv)	9,000	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	E (μv)
0	950.2	1,037.2	1,122.3	1,206.4	1,290.0	1,373.8	1,458.0	1,542.6	1,627.8	0
	8.8	*8.6*	*8.5*	*8.3*	*8.3*	*8.4*	*8.4*	*8.5*	*8.6*	
100	959.0	1,045.8	1,130.8	1,214.7	1,298.3	1,382.2	1,466.4	1,551.1	1,636.4	100
	8.8	*8.6*	*8.4*	*8.4*	*8.4*	*8.4*	*8.4*	*8.5*	*8.5*	
200	967.8	1,054.4	1,139.2	1,223.1	1,306.7	1,390.6	1,474.8	1,559.6	1,644.9	200
	8.7	*8.5*	*8.4*	*8.3*	*8.4*	*8.4*	*8.5*	*8.5*	*8.6*	
300	976.5	1,062.9	1,147.6	1,231.4	1,315.1	1,399.0	1,483.3	1,568.1	1,653.5	300
	8.8	*8.6*	*8.4*	*8.4*	*8.4*	*8.4*	*8.5*	*8.5*	*8.6*	
400	985.3	1,071.5	1,156.0	1,239.8	1,323.5	1,407.4	1,491.8	1,576.6	1,662.1	400
	8.7	*8.5*	*8.4*	*8.4*	*8.3*	*8.4*	*8.4*	*8.5*	*8.6*	
500	994.0	1,080.0	1,164.4	1,248.2	1,331.8	1,415.8	1,500.2	1,585.1	1,670.7	500
	8.7	*8.5*	*8.4*	*8.3*	*8.4*	*8.4*	*8.5*	*8.6*	*8.6*	
600	1,002.7	1,088.5	1,172.8	1,256.5	1,340.2	1,424.2	1,508.7	1,593.7	1,679.3	600
	8.6	*8.5*	*8.4*	*8.4*	*8.4*	*8.5*	*8.5*	*8.5*	*8.6*	
700	1,011.3	1,097.0	1,181.2	1,264.9	1,348.6	1,432.7	1,517.2	1,602.2	1,687.9	700
	8.7	*8.4*	*8.4*	*8.3*	*8.4*	*8.4*	*8.4*	*8.5*	*8.6*	
800	1,020.0	1,105.4	1,189.6	1,273.2	1,357.0	1,441.1	1,525.6	1,610.7	1,696.5	800
	8.6	*8.5*	*8.4*	*8.4*	*8.4*	*8.4*	*8.5*	*8.6*	*8.6*	
900	1,028.6	1,113.9	1,198.0	1,281.6	1,365.4	1,449.5	1,534.1	1,619.3	1,705.1	900
	8.6	*8.4*	*8.4*	*8.4*	*8.4*	*8.5*	*8.5*	*8.5*	*8.6*	
1,000	1,037.2	1,122.3	1,206.4	1,290.0	1,373.8	1,458.0	1,542.6	1,627.8	1,713.7	1,000

Table 2. Reference Table for Pt to Pt – 10 Per Cent Rh Thermocouple.

(Emfs are expressed in microvolts and temperatures in °F. Cold junctions at 32 °F.)

E_t(μv)	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	E (μv)
0	32.0	296.4	509.0	704.7	891.9	1,072 6	1,247.5	1,417.1	1,581.8	0
	31.9	*22.5*	*20.1*	*19.0*	*18.4*	*17.7*	*17.1*	*16.7*	*16.2*	
100	63.9	318.9	529.1	723.7	910.3	1,090.3	1,264.6	1,433.8	1,598.0	100
	30.0	*22.1*	*20.0*	*18.9*	*18.3*	*17.7*	*17.1*	*16.6*	*16.2*	
200	93.9	341.0	549.1	742.6	928.6	1,108.0	1,281.7	1,450.4	1,614.2	200
	28.5	*21.8*	*19.9*	*18.8*	*18.2*	*17.7*	*17.1*	*16.6*	*16.2*	
300	122.4	362.8	569.0	761.4	946.8	1,125.7	1,298.8	1,467.0	1,630.4	300
	27.3	*21.6*	*19.8*	*18.8*	*18.1*	*17.6*	*17.1*	*16.5*	*16.1*	
400	149.7	384.4	588.8	780.2	964.9	1,143.3	1,315.9	1,483.5	1,646.5	400
	26.3	*21.3*	*19.6*	*18.8*	*18.1*	*17.5*	*17.0*	*16.5*	*16.1*	
500	176.0	405.7	608.4	799.0	983.0	1,160.8	1,332.9	1,500.0	1,662.6	500
	25.4	*21.0*	*19.4*	*18.7*	*18.1*	*17.5*	*16.9*	*16.5*	*16.0*	
600	201.4	426.7	627.8	817.7	1,001.1	1,178.3	1,349.8	1,516.5	1,678.6	600
	24.6	*20.9*	*19.3*	*18.6*	*18.0*	*17.4*	*16.9*	*16.4*	*16.0*	
700	226.0	447.6	647.1	836.3	1,019.1	1,195.7	1,366.7	1,532.9	1,694.6	700
	24.0	*20.7*	*19.3*	*18.5*	*17.9*	*17.3*	*16.9*	*16.3*	*16.0*	
800	250.0	468.3	666.4	854.8	1,037.0	1,213.0	1,383.6	1,549.2	1,710.6	800
	23.4	*20.4*	*19.2*	*18.6*	*17.8*	*17.3*	*16.8*	*16.3*	*15.9*	
900	273.4	488.7	685.6	873.4	1,054.8	1,230.3	1,400.4	1,565.5	1,726.5	900
	23.0	*20.3*	*19.1*	*18.5*	*17.8*	*17.2*	*16.7*	*16.3*	*15.9*	
1,000	296.4	509.0	704.7	891.9	1,072.6	1,247.5	1,417.1	1,581.8	1,742.4	1,000

E (μv)	9,000	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	E (μv)
0	1,742.4	1,899.0	2,052.1	2,203.5	2,354.0	2,504.8	2,656.4	2,808.7	2,962.0	0
	15.8	*15.5*	*15.2*	*15.0*	*15.0*	*15.2*	*15.1*	*15.3*	*15.4*	
100	1,758.2	1,914.5	2,067.3	2,218.5	2,369.0	2,520.0	2,671.5	2,824.0	2,977.4	100
	15.8	*15.4*	*15.2*	*15.0*	*15.1*	*15.1*	*15.2*	*15.3*	*15.4*	
200	1,774.0	1,929.9	2,082.5	2,233.5	2,384.1	2,535.1	2,686.7	2,839.3	2,992.8	200
	15.7	*15.4*	*15.2*	*15.0*	*15.1*	*15.1*	*15.2*	*15.3*	*15.5*	
300	1,789.7	1,945.3	2,097.7	2,248.5	2,399.2	2,550.2	2,701.9	2,854.6	3,008.3	300
	15.8	*15.4*	*15.1*	*15.1*	*15.1*	*15.1*	*15.3*	*15.3*	*15.5*	
400	1,805.5	1,960.7	2,112.8	2,263.6	2,414.3	2,565.3	2,717.2	2,869.9	3,023.8	400
	15.7	*15.3*	*15.1*	*15.1*	*15.0*	*15.1*	*15.2*	*15.3*	*15.5*	
500	1,821.2	1,976.0	2,127.9	2,278.7	2,429.3	2,580.4	2,732.4	2,885.2	3,039.3	500
	15.6	*15.3*	*15.1*	*15.0*	*15.1*	*15.2*	*15.3*	*15.4*	*15.4*	
600	1,836.8	1,991.3	2,143.0	2,293.7	2,444.4	2,595.6	2,747.7	2,900.6	3,054.7	600
	15.6	*15.2*	*15.2*	*15.1*	*15.1*	*15.2*	*15.3*	*15.4*	*15.5*	
700	1,852.4	2,006.5	2,158.2	2,308.8	2,459.5	2,610.8	2,763.0	2,916.0	3,070.2	700
	15.6	*15.2*	*15.1*	*15.0*	*15.1*	*15.2*	*15.2*	*15.3*	*15.5*	
800	1,868.0	2,021.7	2,173.3	2,323.8	2,474.6	2,626.0	2,778.2	2,931.3	3,085.7	800
	15.5	*15.2*	*15.1*	*15.1*	*15.1*	*15.2*	*15.2*	*15.4*	*15.5*	
900	1,883.5	2,036.9	2,188.4	2,338.9	2,489.7	2,641.2	2,793.4	2,946.7	3,101.2	900
	15.5	*15.2*	*15.1*	*15.1*	*15.1*	*15.2*	*15.3*	*15.3*	*15.5*	
1,000	1,899.0	2,052.1	2,203.5	2,354.0	2,504.8	2,656.4	2,808.7	2,962.0	3,116.7	1,000

Table 3. Reference Table for Pt to Pt - 13 Per Cent Rh Thermocouple.

(Emfs are expressed in microvolts and temperatures in °C. Cold junctions at 0 °C.)

E (μv)	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	E (μv)
0	0	145.3	258.8	361.0	457.4	549.8	638.3	723.5	806.0	886.1	0
	17.9	*12.2*	*10.6*	*9.9*	*9.5*	*9.0*	*8.7*	*8.4*	*8.1*	*7.9*	
100	17.9	157.5	269.4	370.9	466.9	558.8	647.0	731.9	814.1	894.0	100
	16.7	*12.0*	*10.5*	*9.8*	*9.4*	*9.0*	*8.6*	*8.4*	*8.1*	*7.8*	
200	34.6	169.5	279.9	380.7	476.3	567.8	655.6	740.3	822.2	901.8	200
	15.8	*11.7*	*10.4*	*9.8*	*9.4*	*9.0*	*8.6*	*8.3*	*8.1*	*7.9*	
300	50.4	181.2	290.3	390.5	485.7	576.8	664.2	748.6	830.3	909.7	300
	15.1	*11.5*	*10.3*	*9.7*	*9.3*	*8.9*	*8.6*	*8.3*	*8.0*	*7.8*	
400	65.5	192.7	300.6	400.2	495.0	585.7	672.8	756.9	838.3	917.5	400
	14.5	*11.4*	*10.2*	*9.7*	*9.3*	*8.9*	*8.5*	*8.2*	*8.0*	*7.8*	
500	80.0	204.1	310.8	409.9	504.3	594.6	681.3	765.1	846.3	925.3	500
	13.9	*11.2*	*10.2*	*9.6*	*9.2*	*8.8*	*8.5*	*8.2*	*8.0*	*7.8*	
600	93.9	215.3	321.0	419.5	513.5	603.4	689.8	773.3	854.3	933.1	600
	13.4	*11.1*	*10.1*	*9.5*	*9.1*	*8.8*	*8.5*	*8.2*	*8.0*	*7.8*	
700	107.3	226.4	331.1	429.0	522.6	612.2	698.3	781.5	862.3	940.9	700
	13.0	*10.9*	*10.0*	*9.5*	*9.1*	*8.7*	*8.4*	*8.2*	*8.0*	*7.8*	
800	120.3	237.3	341.1	438.5	531.7	620.9	706.7	789.7	870.3	948.7	800
	12.6	*10.8*	*10.0*	*9.5*	*9.1*	*8.7*	*8.4*	*8.1*	*7.9*	*7.7*	
900	132.9	248.1	351.1	448.0	540.8	629.6	715.1	797.8	878.2	956.4	900
	12.4	*10.7*	*9.9*	*9.4*	*9.0*	*8.7*	*8.4*	*8.2*	*7.9*	*7.7*	
1,000	145.3	258.8	361.0	457.4	549.8	638.3	723.5	806.0	886.1	964.1	1,000

E (μv)	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000	E (μv)
0	964.1	1,040.0	1,113.9	1,186.9	1,259.3	1,331.8	1,404.3	1,476.9	1,550.0	1,623.6	0
	7.6	*7.4*	*7.3*	*7.2*	*7.3*	*7.2*	*7.3*	*7.3*	*7.4*	*7.4*	
100	971.7	1,047.4	1,121.2	1,194.1	1,266.6	1,339.0	1,411.6	1,484.2	1,557.4	1,631.0	100
	7.7	*7.5*	*7.4*	*7.3*	*7.2*	*7.2*	*7.3*	*7.3*	*7.4*	*7.4*	
200	979.4	1,054.9	1,128.6	1,201.4	1,273.8	1,346.2	1,418.9	1,491.5	1,564.8	1,638.4	200
	7.6	*7.4*	*7.3*	*7.3*	*7.3*	*7.3*	*7.2*	*7.3*	*7.3*	*7.4*	
300	987.0	1,062.3	1,135.9	1,208.7	1,281.1	1,353.5	1,426.1	1,498.8	1,572.1	1,645.8	300
	7.7	*7.4*	*7.3*	*7.2*	*7.2*	*7.3*	*7.2*	*7.3*	*7.4*	*7.4*	
400	994.7	1,069.7	1,143.2	1,215.9	1,288.3	1,360.8	1,433.3	1,506.1	1,579.5	1,653.2	400
	7.6	*7.4*	*7.3*	*7.3*	*7.2*	*7.2*	*7.2*	*7.3*	*7.3*	*7.4*	
500	1,002.3	1,077.1	1,150.5	1,223.2	1,295.5	1,368.0	1,440.5	1,513.4	1,586.8	1,660.6	500
	7.6	*7.3*	*7.3*	*7.2*	*7.2*	*7.3*	*7.3*	*7.3*	*7.4*	*7.4*	
600	1,009.9	1,084.4	1,157.8	1,230.4	1,302.7	1,375.3	1,447.8	1,520.7	1,594.2	1,668.0	600
	7.6	*7.4*	*7.3*	*7.2*	*7.2*	*7.3*	*7.2*	*7.3*	*7.3*	*7.4*	
700	1,017.5	1,091.8	1,165.1	1,237.6	1,309.9	1,382.6	1,455.0	1,528.0	1,601.5	1,675.4	700
	7.5	*7.4*	*7.2*	*7.2*	*7.3*	*7.2*	*7.3*	*7.3*	*7.4*	*7.4*	
800	1,025.0	1,099.2	1,172.3	1,244.8	1,317.2	1,389.8	1,462.3	1,535.3	1,608.9	1,682.8	800
	7.5	*7.3*	*7.3*	*7.3*	*7.3*	*7.3*	*7.3*	*7.4*	*7.3*	*7.4*	
900	1,032.5	1,106.5	1,179.6	1,252.1	1,324.5	1,397.1	1,469.6	1,542.7	1,616.2	1,690.2	900
	7.5	*7.4*	*7.3*	*7.2*	*7.3*	*7.2*	*7.3*	*7.3*	*7.4*	*7.4*	
1,000	1,040.0	1,113.9	1,186.9	1,259.3	1,331.8	1,404.3	1,476.9	1,550.0	1,623.6	1,697.6	1,000

Table 4. Reference Table for Pt to Pt-13 Per Cent Rh Thermocouple.

(Emfs are expressed in microvolts and temperatures in °F. Cold junctions at 32 °F.)

E (μv)	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	E (μv)
0	32.0 *32.2*	293.5 *22.0*	497.8 *19.1*	681.8 *17.8*	855.3 *17.0*	1,021.6 *16.2*	1,180.9 *15.6*	1,334.3 *15.1*	1,482.8 *14.6*	1,627.0 *14.2*	0
100	64.2 *30.1*	315.5 *21.6*	516.9 *18.9*	699.6 *17.7*	872.3 *17.0*	1,037.8 *16.2*	1,196.5 *15.6*	1,349.4 *15.1*	1,497.4 *14.6*	1,641.2 *14.1*	100
200	94.3 *28.4*	337.1 *21.1*	535.8 *18.7*	717.3 *17.6*	889.3 *16.9*	1,054.0 *16.2*	1,212.1 *15.5*	1,364.5 *15.0*	1,512.0 *14.5*	1,655.3 *14.1*	200
300	122.7 *27.2*	358.2 *20.7*	554.5 *18.6*	734.9 *17.5*	906.2 *16.8*	1,070.2 *16.1*	1,227.6 *15.4*	1,379.5 *14.9*	1,526.5 *14.4*	1,669.4 *14.1*	300
400	149.9 *26.1*	378.9 *20.4*	573.1 *18.4*	752.4 *17.4*	923.0 *16.7*	1,086.3 *16.0*	1,243.0 *15.3*	1,394.4 *14.8*	1,540.9 *14.4*	1,683.5 *14.0*	400
500	176.0 *25.0*	399.3 *20.2*	591.5 *18.3*	769.8 *17.3*	939.7 *16.6*	1,102.3 *15.9*	1,258.3 *15.3*	1,409.2 *14.8*	1,555.3 *14.4*	1,697.5 *14.1*	500
600	201.0 *24.1*	419.5 *20.0*	609.8 *18.2*	787.1 *17.2*	956.3 *16.4*	1,118.2 *15.8*	1,273.6 *15.3*	1,424.0 *14.8*	1,569.7 *14.4*	1,711.6 *14.0*	600
700	225.1 *23.4*	439.5 *19.7*	628.0 *18.0*	804.3 *17.1*	972.7 *16.4*	1,134.0 *15.7*	1,288.9 *15.2*	1,438.8 *14.7*	1,584.1 *14.4*	1,725.6 *14.0*	700
800	248.5 *22.7*	459.2 *19.4*	646.0 *18.0*	821.4 *17.0*	989.1 *16.3*	1,149.7 *15.6*	1,304.1 *15.1*	1,453.5 *14.6*	1,598.5 *14.3*	1,739.6 *13.9*	800
900	271.2 *22.3*	478.6 *19.2*	664.0 *17.8*	838.4 *16.9*	1,005.4 *16.2*	1,165.3 *15.6*	1,319.2 *15.1*	1,468.1 *14.7*	1,612.8 *14.2*	1,753.5 *13.9*	900
1,000	293.5	497.8	681.8	855.3	1,021.6	1,180.9	1,334.3	1,482.8	1,627.0	1,767.4	1,000

E (μv)	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000	E (μv)
0	1,767.4 *13.8*	1,904.0 *13.4*	2,037.0 *13.2*	2,168.4 *13.0*	2,298.7 *13.1*	2,429.2 *13.0*	2,559.7 *13.1*	2,690.4 *13.2*	2,822.0 *13.3*	2,954.5 *13.3*	0
100	1,781.2 *13.7*	1,917.4 *13.4*	2,050.2 *13.2*	2,181.4 *13.1*	2,311.8 *13.0*	2,442.2 *13.0*	2,572.8 *13.1*	2,703.6 *13.1*	2,835.3 *13.3*	2,967.8 *13.3*	100
200	1,794.9 *13.7*	1,930.8 *13.3*	2,063.4 *13.2*	2,194.5 *13.1*	2,324.8 *13.1*	2,455.2 *13.1*	2,585.9 *13.0*	2,716.7 *13.1*	2,848.6 *13.2*	2,981.1 *13.3*	200
300	1,808.6 *13.8*	1,944.1 *13.3*	2,076.6 *13.2*	2,207.6 *13.0*	2,337.9 *13.0*	2,468.3 *13.1*	2,598.9 *13.0*	2,729.8 *13.2*	2,861.8 *13.3*	2,994.4 *13.4*	300
400	1,822.4 *13.7*	1,957.4 *13.3*	2,089.8 *13.1*	2,220.6 *13.1*	2,350.9 *13.0*	2,481.4 *13.0*	2,611.9 *13.0*	2,743.0 *13.1*	2,875.1 *13.2*	3,007.8 *13.3*	400
500	1,836.1 *13.7*	1,970.7 *13.3*	2,102.9 *13.1*	2,233.7 *13.0*	2,363.9 *13.0*	2,494.4 *13.1*	2,624.9 *13.1*	2,756.1 *13.2*	2,888.3 *13.3*	3,021.1 *13.3*	500
600	1,849.8 *13.6*	1,984.0 *13.3*	2,116.0 *13.1*	2,246.7 *13.0*	2,376.9 *13.0*	2,507.5 *13.1*	2,638.0 *13.0*	2,769.3 *13.1*	2,901.6 *13.2*	3,034.4 *13.3*	600
700	1,863.4 *13.6*	1,997.3 *13.3*	2,129.1 *13.1*	2,259.7 *13.0*	2,389.9 *13.1*	2,520.6 *13.0*	2,651.0 *13.1*	2,782.4 *13.2*	2,914.8 *13.2*	3,047.7 *13.3*	700
800	1,877.0 *13.5*	2,010.6 *13.2*	2,142.2 *13.1*	2,272.7 *13.0*	2,403.0 *13.1*	2,533.6 *13.1*	2,664.1 *13.1*	2,795.6 *13.2*	2,928.0 *13.2*	3,061.0 *13.4*	800
900	1,890.5 *13.5*	2,023.8 *13.2*	2,155.3 *13.1*	2,285.7 *13.0*	2,416.1 *13.1*	2,546.7 *13.0*	2,677.2 *13.2*	2,808.8 *13.2*	2,941.2 *13.3*	3,074.4 *13.3*	900
1,000	1,904.0	2,037.0	2,168.4	2,298.7	2,429.2	2,559.7	2,690.4	2,822.0	2,954.5	3,087.7	1,000

Table 5. Standard Centigrade Table for Chromel-Alumel Thermocouples.

Temperature (°C)	Electromotive force in millivolts (reference junction at 0 °C)										
	0	10	20	30	40	50	60	70	80	90	100
−200	−5.75	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
−100	−3.49	−3.78	−4.05	−4.32	−4.57	−4.81	−5.03	−5.24	−5.43	−5.60	−5.75
− 0	0.00	−.39	−.77	−1.14	−1.50	−1.86	−2.21	−2.55	−2.87	−3.19	−3.49
0	0.00	0.40	0.80	1.20	1.61	2.02	2.43	2.85	3.26	3.68	4.10
100	4.10	4.51	4.92	5.33	5.73	6.13	6.53	6.93	7.33	7.73	8.13
200	8.13	8.53	8.93	9.34	9.74	10.15	10.56	10.97	11.38	11.80	12.21
300	12.21	12.62	13.04	13.45	13.87	14.29	14.71	15.13	15.55	15.97	16.39
400	16.39	16.82	17.24	17.66	18.08	18.50	18.93	19.36	19.78	20.21	20.64
500	20.64	21.07	21.49	21.92	22.34	22.77	23.20	23.62	24.05	24.48	24.90
600	24.90	25.33	25.75	26.18	26.60	27.03	27.45	27.87	28.29	28.72	29.14
700	29.14	29.56	29.98	30.40	30.82	31.23	31.65	32.07	32.48	32.90	33.31
800	33.31	33.71	34.12	34.53	34.94	35.35	35.75	36.16	36.56	36.96	37.36
900	37.36	37.76	38.16	38.56	38.96	39.35	39.75	40.14	40.53	40.92	41.31
1,000	41.31	41.70	42.08	42.47	42.86	43.24	43.62	44.00	44.38	44.76	45.14
1,100	45.14	45.52	45.89	46.27	46.64	47.01	47.38	47.75	48.12	48.48	48.85
1,200	48.85	49.21	49.57	49.94	50.29	50.65	51.00	51.36	51.71	52.06	52.41
1,300	52.41	52.75	53.10	53.45	53.79	54.13	54.47	54.81	55.15	55.48	55.81
1,400	55.81	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

Table 6. Standard Fahrenheit Table for Chromel-Alumel Thermocouples.

Temperature (°F)	Electromotive force in millivolts (reference junction at 32 °F)										
	0	10	20	30	40	50	60	70	80	90	100
−300	−5.51	−5.60	.....	.....	.....	.....	.....	.....	.....	.....	.....
−200	−4.29	−4.43	−4.57	−4.71	−4.84	−4.96	−5.08	−5.19	−5.30	−5.41	−5.51
−100	−2.65	−2.83	−3.01	−3.19	−3.36	−3.52	−3.68	−3.84	−4.00	−4.15	−4.29
− 0	−0.68	−0.89	−1.10	−1.30	−1.50	−1.70	−1.90	−2.09	−2.28	−2.47	−2.65
0	−0.68	−0.47	−0.26	−0.04	+0.18	0.40	0.62	0.84	1.06	1.29	1.52
100	1.52	1.74	1.97	2.20	2.43	2.66	2.89	3.12	3.36	3.59	3.82
200	3.82	4.05	4.28	4.51	4.74	4.97	5.19	5.42	5.64	5.87	6.09
300	6.09	6.31	6.53	6.75	6.98	7.20	7.42	7.64	7.87	8.09	8.31
400	8.31	8.53	8.76	8.98	9.20	9.43	9.66	9.88	10.11	10.33	10.56
500	10.56	10.79	11.02	11.25	11.47	11.70	11.93	12.16	12.39	12.62	12.85
600	12.85	13.08	13.31	13.55	13.78	14.01	14.24	14.48	14.71	14.94	15.18
700	15.18	15.41	15.64	15.88	16.11	16.35	16.58	16.82	17.05	17.29	17.52
800	17.52	17.75	17.99	18.22	18.46	18.70	18.93	19.17	19.41	19.64	19.88
900	19.88	20.12	20.36	20.59	20.83	21.07	21.30	21.54	21.78	22.01	22.25
1,000	22.25	22.49	22.72	22.96	23.20	23.43	23.67	23.91	24.14	24.38	24.62
1,100	24.62	24.85	25.09	25.33	25.57	25.80	26.04	26.27	26.51	26.74	26.98
1,200	26.98	27.21	27.45	27.68	27.92	28.15	28.39	28.62	28.86	29.09	29.33
1,300	29.33	29.56	29.79	30.02	30.26	30.49	30.72	30.96	31.19	31.42	31.65
1,400	31.65	31.88	32.11	32.34	32.57	32.80	33.03	33.26	33.49	33.71	33.94
1,500	33.94	34.17	34.40	34.62	34.85	35.08	35.30	35.53	35.75	35.98	36.20
1,600	36.20	36.42	36.65	36.87	37.10	37.32	37.54	37.76	37.99	38.21	38.43
1,700	38.43	38.65	38.87	39.09	39.31	39.53	39.75	39.96	40.18	40.40	40.62
1,800	40.62	40.83	41.05	41.27	41.48	41.70	41.91	42.13	42.34	42.56	42.77
1,900	42.77	42.98	43.20	43.41	43.62	43.83	44.04	44.26	44.47	44.68	44.89
2,000	44.89	45.10	45.31	45.52	45.73	45.93	46.14	46.35	46.56	46.76	46.97
2,100	46.97	47.18	47.38	47.59	47.79	47.99	48.20	48.40	48.61	48.81	49.01
2,200	49.01	49.21	49.41	49.61	49.81	50.01	50.21	50.41	50.61	50.80	51.00
2,300	51.00	51.20	51.39	51.59	51.78	51.98	52.17	52.37	52.56	52.75	52.95
2,400	52.95	53.14	53.33	53.52	53.71	53.90	54.09	54.28	54.47	54.66	54.85
2,500	54.85	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

Table 7. Corresponding Values of Temperature and Electromotive Force for Iron-Constantan Thermocouples.

(Reference junctions at 0 °C.)

Temperature (°C)	Emf (mv)	Temperature (°C)	Emf (mv)	Temperature (°C)	Emf (mv)	Temperature (°C)	Emf (mv)
		0	0.00	400	22.07	800	45.72
		10	0.52	410	22.62	810	46.37
		20	1.05	420	23.17	820	47.03
		30	1.58	430	23.72	830	47.69
		40	2.12	440	24.27	840	48.34
		50	2.66	450	24.82	850	49.00
		60	3.20	460	25.37	860	49.66
		70	3.75	470	25.92	870	50.32
		80	4.30	480	26.47	880	50.97
		90	4.85	490	27.03	890	51.63
		100	5.40	500	27.58	900	52.29
		110	5.95	510	28.14	910	52.88
		120	6.51	520	28.70	920	53.47
		130	7.07	530	29.26	930	54.06
		140	7.63	540	29.82	940	54.65
		150	8.19	550	30.39	950	55.25
		160	8.75	560	30.96	960	55.84
		170	9.31	570	31.53	970	56.43
		180	9.87	580	32.11	980	57.03
		190	10.43	590	32.69	990	57.63
-200	-8.27	200	10.99	600	33.27	1,000	58.22
-190	-8.02	210	11.56	610	33.86		
-180	-7.75	220	12.12	620	34.45		
-170	-7.46	230	12.68	630	35.04		
-160	-7.14	240	13.23	640	35.64		
-150	-6.80	250	13.79	650	36.24		
-140	-6.44	260	14.35	660	36.84		
-130	-6.06	270	14.90	670	37.45		
-120	-5.66	280	15.46	680	38.06		
-110	-5.25	290	16.01	690	38.68		
-100	-4.82	300	16.56	700	39.30		
-90	-4.38	310	17.12	710	39.93		
-80	-3.93	320	17.67	720	40.56		
-70	-3.47	330	18.22	730	41.19		
-60	-3.00	340	18.77	740	41.83		
-50	-2.52	350	19.32	750	42.48		
-40	-2.03	360	19.87	760	43.12		
-30	-1.53	370	20.42	770	43.77		
-20	-1.03	380	20.97	780	44.42		
-10	-0.52	390	21.52	790	45.07		
0	0.00	400	22.07	800	45.72		

Table 8. Corresponding Values of Temperature and Electromotive Force for Iron-Constantan Thermocouples.

(Reference junctions at 32 °F.)

Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)
		0	-0.92	500	14.35	1,000	29.70	1,500	46.74
		10	-.63	510	14.65	1,010	30.01	1,510	47.10
		20	-.35	520	14.96	1,020	30.33	1,520	47.47
		30	-.06	530	15.27	1,030	30.64	1,530	47.83
		40	+.23	540	15.58	1,040	30.96	1,540	48.20
		50	.52	550	15.89	1,050	31.28	1,550	48.56
		60	.82	560	16.20	1,060	31.60	1,560	48.93
		70	1.11	570	16.50	1,070	31.92	1,570	49.29
		80	1.41	580	16.81	1,080	32.24	1,580	49.66
		90	1.70	590	17.12	1,090	32.56	1,590	50.02
		100	2.00	600	17.43	1,100	32.88	1,600	50.39
		110	2.30	610	17.73	1,110	33.20	1,610	50.75
		120	2.60	620	18.04	1,120	33.53	1,620	51.12
		130	2.90	630	18.34	1,130	33.86	1,630	51.49
		140	3.20	640	18.65	1,140	34.18	1,640	51.85
		150	3.50	650	18.95	1,150	34.51	1,650	52.22
		160	3.81	660	19.26	1,160	34.84	1,660	52.55
		170	4.11	670	19.56	1,170	35.17	1,670	52.88
		180	4.42	680	19.87	1,180	35.50	1,680	53.21
		190	4.72	690	20.18	1,190	35.84	1,690	53.54
-300	-7.87	200	5.03	700	20.48	1,200	36.17	1,700	53.87
-290	-7.72	210	5.34	710	20.79	1,210	36.50	1,710	54.20
-280	-7.55	220	5.64	720	21.09	1,220	36.84	1,720	54.52
-270	-7.38	230	5.95	730	21.40	1,230	37.18	1,730	54.85
-260	-7.20	240	6.26	740	21.70	1,240	37.52	1,740	55.18
-250	-7.02	250	6.57	750	22.01	1,250	37.86	1,750	55.51
-240	-6.83	260	6.88	760	22.31	1,260	38.20	1,760	55.84
-230	-6.63	270	7.19	770	22.62	1,270	38.54	1,770	56.17
-220	-6.43	280	7.50	780	22.92	1,280	38.88	1,780	56.50
-210	-6.22	290	7.81	790	23.23	1,290	39.23	1,790	56.83
-200	-6.01	300	8.12	800	23.53	1,300	39.58	1,800	57.16
-190	-5.79	310	8.43	810	23.84	1,310	39.93		
-180	-5.57	320	8.75	820	24.14	1,320	40.28		
-170	-5.34	330	9.06	830	24.45	1,330	40.63		
-160	-5.11	340	9.37	840	24.75	1.340	40.98		
-150	-4.87	350	9.68	850	25.06	1,350	41.34		
-140	-4.63	360	10.00	860	25.37	1,360	41.69		
-130	-4.38	370	10.31	870	25.67	1,370	42.05		
-120	-4.13	380	10.62	880	25.98	1,380	42.40		
-110	-3.88	390	10.93	890	26.29	1,390	42.76		
-100	-3.63	400	11.24	900	26.59	1,400	43.12		
-90	-3.37	410	11.56	910	26.90	1,410	43.48		
-80	-3.11	420	11.87	920	27.21	1,420	43.84		
-70	-2.85	430	12.18	930	27.52	1,430	44.20		
-60	-2.58	440	12.49	940	27.83	1,440	44.56		
-50	-2.31	450	12.80	950	28.14	1,450	44.92		
-40	-2.04	460	13.11	960	28.45	1,460	45.28		
-30	-1.76	470	13.42	970	28.76	1,470	45.65		
-20	-1.48	480	13.73	980	29.07	1,480	46.01		
-10	-1.20	490	14.04	990	29.39	1,490	46.37		
0	-0.92	500	14.35	1,000	29.70	1,500	46.74		

Table 9. Corresponding Values of Temperature and Electromotive Force of Copper-Constantan Thermocouples as Derived from Adams' Table.

(Reference junctions at 0 °C.)

Temperature (°C)	Emf (mv)	Temperature (°C)	Emf (mv)	Temperature (°C)	Emf (mv)
-200	-5.539	0	0.000	200	9.285
-190	-5.378	10	.389	210	9.820
-180	-5.204	20	.787	220	10.360
-170	-5.016	30	1.194	230	10.905
-160	-4.815	40	1.610	240	11.455
-150	-4.602	50	2.034	250	12.010
-140	-4.376	60	2.467	260	12.571
-130	-4.137	70	2.908	270	13.136
-120	-3.886	80	3.356	280	13.706
-110	-3.623	90	3.812	290	14.280
-100	-3.349	100	4.276	300	14.859
- 90	-3.063	110	4.747	310	15.443
- 80	-2.765	120	5.225	320	16.030
- 70	-2.456	130	5.710	330	16.621
- 60	-2.137	140	6.202	340	17.216
- 50	-1.807	150	6.700	350	17.815
- 40	-1.466	160	7.205	360	18.418
- 30	-1.114	170	7.716	370	19.025
- 20	-0.752	180	8.233	380	19.635
- 10	-0.381	190	8.756	390	20.248
0	.000	200	9.285	400	20.865

Table 10. Corresponding Values of Temperature and Electromotive Force for Copper-Constantan Thermocouples as Derived from Adams' Table.

(Reference junctions at 32 °F.)

Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)	Temperature (°F)	Emf (mv)
−300	−5.283	0	−0.671	300	6.644	600	15.769
−290	−5.184	10	− .464	310	6.924	610	16.096
−280	−5.081	20	− .255	320	7.206	620	16.424
−270	−4.973	30	− .043	330	7.489	630	16.753
−260	−4.861	40	+ .172	340	7.774	640	17.084
−250	−4.745	50	.390	350	8.061	650	17.416
−240	−4.626	60	.610	360	8.350	660	17.749
−230	−4.503	70	.832	370	8.640	670	18.083
−220	−4.376	80	1.057	380	8.932	680	18.418
−210	−4.245	90	1.285	390	9.226	690	18.754
−200	−4.110	100	1.516	400	9.521	700	19.091
−190	−3.971	110	1.750	410	9.819	710	19.430
−180	−3.829	120	1.987	420	10.119	720	19.770
−170	−3.683	130	2.226	430	10.420	730	20.111
−160	−3.533	140	2.467	440	10.722	740	20.453
−150	−3.380	150	2.711	450	11.026	750	20.796
−140	−3.223	160	2.957	460	11.332		
−130	−3.062	170	3.206	470	11.639		
−120	−2.898	180	3.457	480	11.948		
−110	−2.731	190	3.710	490	12.259		
−100	−2.560	200	3.966	500	12.571		
− 90	−2.386	210	4.224	510	12.885		
− 80	−2.209	220	4.484	520	13.200		
− 70	−2.028	230	4.747	530	13.516		
− 60	−1.844	240	5.012	540	13.833		
− 50	−1.656	250	5.279	550	14.152		
− 40	−1.465	260	5.548	560	14.472		
− 30	−1.271	270	5.819	570	14.794		
− 20	−1.074	280	6.092	580	15.118		
− 10	−0.874	290	6.367	590	15.443		
0	− .671	300	6.644	600	15.769		

Table 11. Thermal Emf of Important Thermocouple Materials Relative to Platinum.

Temp. (°C)	Chromel P (mv)	Alumel (mv)	Copper (mv)	Iron (mv)	Constantan (mv)
−200	−3.36	+2.39	−0.19	−2.92	+5.35
−100	−2.20	+1.29	−0.37	−1.84	+2.98
0	0	0	0	0	0
+100	+2.81	−1.29	+0.76	+1.89	−3.51
200	5.96	−2.17	1.83	3.54	−7.45
300	9.32	−2.89	3.15	4.85	−11.71
400	12.75	−3.64	4.68	5.88	−16.19
500	16.21	−4.43	6.41	6.79	−20.79
600	19.62	−5.28	8.34	7.80	−25.47
700	22.96	−6.18	10.49	9.12	−30.18
800	26.23	−7.08	12.84	10.86	−34.86
900	29.41	−7.95	15.41	12.84	−39.45
1000	32.52	−8.79	18.20	14.30	−43.92
1100	35.56	−9,58	......	......	......
1200	*38.51*	*−10.34*	......	......	......
1300	41.35	−11.06	......	......	......
1400	44.04	−11.77	......	......	......

Table 12. Thermal Emf[a] of Chemical Elements Relative to Platinum. [A positive sign means that in a simple thermoelectric circuit the resultant emf given is in such a direction as to produce a current from the element to the platinum at the reference junction (0 °C)].

Temp. (°C)	Lithium (mv)	Sodium (mv)	Potassium (mv)	Rubidium (mv)	Cesium (mv)	Calcium (mv)	Cerium (mv)
−200	−1.12	+1.00	+1.61	+1.09	+0.22	......	......
−100	−1.00	+0.29	+0.78	+0.46	−0.13	......	......
0	0	0	0	0	0	0	0
+100	+1.82	......	......	......	......	−0.51	+1.14
200	......	......	......	......	......	−1.13	2.46
300	......	......	......	......	......	−1.85	......

Temp. (°C)	Magnesium (mv)	Zinc (mv)	Cadmium (mv)	Mercury (mv)	Indium (mv)	Thallium (mv)	Aluminum (mv)
−200	+0.37	−0.07	−0.04	......	......	......	+0.45
−100	−0.09	−0.33	−0.31	......	......	......	−0.06
0	0	0	0	0	0	0	0
+100	+0.44	+0.76	+0.90	−0.60	+0.69	+0.58	+0.42
200	+1.10	1.89	2.35	−1.33	......	1.30	1.06
300	......	3.42	4.24	......	......	2.16	1.88
400	......	5.29	......	......	......	......	2.84
500	......	......	......	......	......	......	3.93
600	......	......	......	......	......	......	5.15

Temp. (°C)	Carbon (mv)	Silicon (mv)	Germanium (mv)	Tin (mv)	Lead (mv)	Antimony (mv)	Bismuth (mv)
−200	......	+63.13	−46.00	+0.26	+0.24	......	+12.39
−100	......	+37.17	−26.62	−0.12	−0.13	......	+7.54
0	0	0	0	0	0	0	0
+100	+0.70	−41.56	+33.9	+0.42	+0.44	+4.89	−7.34
200	1.54	−80.58	72.4	1.07	1.09	10.14	−13.57
300	2.55	−110.09	91.8	......	1.91	15.44	......
400	3.72	......	82.3	......	......	20.53	......
500	5.15	......	63.5	......	......	25.10	......
600	6.79	......	43.9	......	......	28.88	......
700	8.84	......	27.9	......	......	......	......
800	11.01	......	......	......	......	......	......
900	13.59	......	......	......	......	......	......
1000	16.51	......	......	......	......	......	......
1100	19.49	......	......	......	......	......	......

Temp. (°C)	Copper (mv)	Silver (mv)	Gold (mv)	Iron (mv)	Cobalt (mv)	Nickel (mv)
−200	−0.19	−0.21	−0.21	−3.10	......	+2.28
−100	−0.37	−0.39	−0.39	−1.94	......	+1.22
0	0	0	0	0	0	0
+100	+0.76	+0.74	+0.78	+1.98	−1.33	−1.48
200	1.83	1.77	1.84	3.69	−3.08	−3.10
300	3.15	3.05	3.14	5.03	−5.10	−4.59
400	4.68	4.57	4.63	6.08	−7.24	−5.45
500	6.41	6.36	6.29	7.00	−9.35	−6.16
600	8.34	8.41	8.12	8.02	−11.28	−7.04
700	10.49	10.75	10.13	9.34	−12.88	−8.10
800	12.84	13.36	12.29	11.09	−14.00	−9.35
900	15.41	16.20	14.61	13.10	−14.49	−10.69
1000	18.20	......	17.09	14.64	−14.20	−12.13
1100	......	......	......	......	−12.98	−13.62
1200	......	......	......	......	−10.68	......

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[a] The values below 0 °C, in most cases, have not been determined on the same samples as the values above 0 °C.

Table 12.—(*Continued*).

Temp. (°C)	Iridium (mv)	Rhodium (mv)	Palladium (mv)	Molybdenum (mv)	Tungsten (mv)	Tantalum (mv)	Thorium (mv)
-200	-0.25	-0.20	+0.81	......	+0.43	+0.21	......
-100	-0.35	-0.34	+0.48	......	-0.15	-0.10	......
0	0	0	0	0	0	0	0
+100	+0.65	+0.70	-0.57	+1.45	+1.12	+0.33	-0.13
200	1.49	1.61	-1.23	3.19	2.62	0.93	-0.26
300	2.47	2.68	-1.99	5.23	4.48	1.79	-0.40
400	3.55	3.91	-2.82	7.57	6.70	2.91	-0.50
500	4.78	5.28	-3.84	10.20	9.30	4.30	-0.53
600	6.10	6.77	-5.03	13.13	12.26	5.95	-0.45
700	7.56	8.40	-6.41	16.35	15.60	7.87	-0.21
800	9.12	10.16	-7.98	19.87	19.30	10.05	+0.22
900	10.80	12.04	-9.72	23.69	23.36	12.49	+0.87
1000	12.59	14.05	-11.63	27.80	27.80	15.20	+1.73
1100	14.48	16.18	-13.70	32.21	32.60	18.17	+2.80
1200	16.47	18.42	-15.89	36.91	37.78	21.41	+4.04
1300	18.47	20.70	-18.12	......	......	......	+5.42
1400	20.48	23.00	-20.41	......	......	......	......
1500	22.50	25.35	-22.74	......	......	......	......

Table 13. Thermal Emf of Some Alloys Relative to Platinum.

Temp. (°C)	Manganin (mv)	Gold-Chromium (mv)	Copper-Beryllium (mv)	Yellow Brass (mv)	Phospher Bronze (mv)	Solder 50Sn-50Pb (mv)	Solder 96.5Sn-3.5Ag (mv)
0	0	0	0	0	0	0	0
+100	+0.61	-0.17	+0.67	+0.60	+0.55	+0.46	+0.45
200	1.55	-0.32	1.62	1.49	1.34	......	......
300	2.77	-0.44	2.81	2.58	2.34	......	......
400	4.25	-0.55	4.19	3.85	3.50	......	......
500	5.95	-0.63	......	5.30	4.81	......	......
600	7.84	-0.66	......	6.96	6.30	......	......

Temp. (°C)	18-8 Stainless steel (mv)	Spring steel (mv)	80Ni-20Cr (mv)	60Ni-24Fe-16Cr (mv)	Copper coin (95Cu-4Sn-1Zn) (mv)	Nickel coin (75Cu-25Ni) (mv)	Silver coin (90Ag-10Cu) (mv)
0	0	0	0	0	0	0	0
+100	+0.44	+1.32	+1.14	+0.85	+0.60	-2.76	+0.80
200	1.04	2.63	2.62	2.01	1.48	-6.01	1.90
300	1.76	3.81	4.34	3.41	2.60	-9.71	3.25
400	2.60	4.84	6.25	5.00	3.91	-13.78	4.81
500	3.56	5.80	8.31	6.76	5.44	-18.10	6.59
600	4.67	6.86	10.53	8.68	7.14	-22.59	8.64
700	5.93	......	12.91	10.78	......	......	......
800	7.37	......	15.44	13.06	......	......	......
900	8.99	......	18.11	15.50	......	......	......
1000	......	......	20.91	18.10	......	......	......

Table 14. Thermal Emf of Alloys Relative to Platinum with Junctions at 0 and 100 °C.

Tin-lead by weight	Emf (mv)	Tin-copper by weight	Emf (mv)	Zinc-copper by weight	Emf (mv)
0Sn-100Pb	+0.44	0Sn-100Cu	+0.76	0Zn-100Cu	+0.76
10Sn-90Pb	+0.44	10Sn-90Cu	+0.53	10Zn-90Cu	+0.54
20Sn-80Pb	+0.44	20Sn-80Cu	+0.56	20Zn-80Cu	+0.53
30Sn-70Pb	+0.44	30Sn-70Cu	+0.65	30Zn-70Cu	+0.54
40Sn-60Pb	+0.45	40Sn-60Cu	+0.65	40Zn-60Cu	+0.51
50Sn-50Pb	+0.45	50Sn-50Cu	+0.69	50Zn-50Cu	+0.54
60Sn-40Pb	+0.44	60Sn-40Cu	+0.72	60Zn-40Cu	+0.47
70Sn-30Pb	+0.44	70Sn-30Cu	+0.62	70Zn-30Cu	+0.87
80Sn-20Pb	+0.43	80Sn-20Cu	+0.54	80Zn-20Cu	+0.66
90Sn-10Pb	+0.42	90Sn-10Cu	+0.48	90Zn-10Cu	+0.98
100Sn-0Pb	+0.42	100Sn-0Cu	+0.42	100Zn-0Cu	+0.76

Gold-silver by weight	Emf (mv)	Gold-palladium by weight	Emf (mv)	Nickel-copper by weight	Emf (mv)
0Au-100Ag	+0.74	0Au-100Pd	−0.57	0Ni-100Cu	+0.76
10Au-90Ag	+0.55	10Au-90Pd	−0.85	10Ni-90Cu	−2.63
20Au-80Ag	+0.48	20Au-80Pd	−1.25	20Ni-80Cu	−3.08
30Au-70Ag	+0.47	30Au-70Pd	−1.42	30Ni-70Cu	−3.54
40Au-60Ag	+0.47	40Au-60Pd	−1.69	40Ni-60Cu	−4.03
50Au-50Ag	+0.48	50Au-50Pd	−2.44	50Ni-50Cu	−3.64
60Au-40Ag	+0.49	60Au-40Pd	−2.97	60Ni-40Cu	−3.06
70Au-30Ag	+0.49	70Au-30Pd	−2.63	70Ni-30Cu	−2.54
80Au-20Ag	+0.50	80Au-20Pd	−0.46	80Ni-20Cu	−2.49
90Au-10Ag	+0.59	90Au-10Pd	−0.05	90Ni-10Cu	−1.93
100Au-0Ag	+0.78	100Au-0Pd	+0.78	100Ni-0Cu	−1.48

Tin-bismuth by weight	Emf (mv)	Antimony-cadmium by weight	Emf (mv)	Antimony-bismuth by weight	Emf (mv)
0Sn-100Bi	−7.34	0Sb-100Cd	+0.90	0Sb-100Bi	−7.34
10Sn-90Bi	+4.00	10Sb-90Cd	+1.52	10Sb-90Bi	−8.82
20Sn-80Bi	+3.52	20Sb-80Cd	+2.88	20Sb-80Bi	−7.31
30Sn-70Bi	+2.56	30Sb-70Cd	+ 6.4	30Sb-70Bi	−5.66
40Sn-60Bi	+2.10	40Sb-60Cd	+12.2	40Sb-60Bi	−4.05
50Sn-50Bi	+1.77	50Sb-50Cd	+23.1	50Sb-50Bi	−2.51
60Sn-40Bi	+1.14	60Sb-40Cd	+44.4	60Sb-40Bi	−1.06
70Sn-30Bi	+0.95	70Sb-30Cd	+21.5	70Sb-30Bi	+0.32
80Sn-20Bi	+0.78	80Sb-20Cd	+12.8	80Sb-20Bi	+1.79
90Sn-10Bi	+0.60	90Sb-10Cd	+ 8.1	90Sb-10Bi	+3.31
100Sn-0Bi	+0.42	100Sb-0Cd	+4.89	100Sb-0Bi	+4.89

Table 15[a]. Electrical Resistivity as a Function of Temperature. [At 0 °C both the relative (Rt/Ro) and actual resistivity (microhm-cm) are given.]

Temp. (°C)	Platinum (R_t/R_o)	Copper (R_t/R_o)	Nickel (R_t/R_o)	Iron (R_t/R_o)	Silver (R_t/R_o)	90% Pt-10% Rh (R_t/R_o)	87% Pt-13% Rh (R_t/R_o)
−200	0.177	0.117	.....	.....	0.176	.....	.....
−100	0.599	0.557	.....	.....	0.596	.....	.....
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	(9.83)	(1.56)	(6.38)	(8.57)	(1.50)	(18.4)	(19.0)
+100	1.392	1.431	1.663	1.650	1.408	1.166	1.156
200	1.773	1.862	2.501	2.464	1.827	1.330	1.308
300	2.142	2.299	3.611	3.485	2.256	1.490	1.456
400	2.499	2.747	4.847	4.716	2.698	1.646	1.601
500	2.844	3.210	5.398	6.162	3.150	1.798	1.744
600	3.178	3.695	5.882	7.839	3.616	1.947	1.885
700	3.500	4.208	6.327	9.790	4.094	2.093	2.023
800	3.810	4.752	6.751	12.009	4.586	2.234	2.157
900	4.109	5.334	7.156	12.790	5.091	2.370	2.287
1000	4.396	5.960	7.542	13.070	.....	2.503	2.414
1100	4.671	.....	.....	.....	.....	2.633	2.538
1200	4.935	.....	.....	.....	.....	2.761	2.660
1300	5.187	.....	.....	.....	.....	2.887	2.780
1400	5.427	.....	.....	.....	.....	3.011	2.898
1500	5.655	.....	.....	.....	.....	3.133	3.014

Temp. (°C)	80Ni-20Cr (R_t/R_o)	60Ni-24Fe-16Cr (R_t/R_o)	50Fe-30Ni-20Cr (R_t/R_o)	Chromel P (90Ni-10Cr) (R_t/R_o)	Alumel 95Ni-Bal Al Si and Mn (R_t/R_o)	Constantan (55 Cu-45Ni) (R_t/R_o)	Manganin (R_t/R_o)
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	(107.6)	(111.6)	(99.0)	(70.0)	(28.1)	(48.9)	(48.2)
100	1.021	1.025	1.037	1.041	1.239	0.999	1.002
200	1.041	1.048	1.073	1.086	1.428	0.996	0.996
300	1.056	1.071	1.107	1.134	1.537	0.994	0.991
400	1.068	1.092	1.137	1.187	1.637	0.994	0.983
500	1.073	1.108	1.163	1.222	1.726	1.007	.....
600	1.071	1.115	1.185	1.248	1.814	1.024	.....
700	1.067	1.119	1.204	1.275	1.899	1.040	.....
800	1.066	1.127	1.221	1.304	1.982	1.056	.....
900	1.071	1.138	1.237	1.334	2.066	1.074	.....
1000	1.077	1.149	1.251	1.365	2.150	1.092	.....
1100	1.083	.....	.....	1.397	2.234	1.110	.....
1200	.....	.....	.....	1.430	2.318	.....	.....

[a] The values below 0 °C, in most cases, have not been determined on the same samples as the values above 0 °C.

Table 16. Spectral Emissivity of Materials, Surface Unoxidized.

Element	$\epsilon_{0.65\mu}$	
	Solid	Liquid
Beryllium	0.61	0.61
Carbon	0.80–0.93	...
Chromium	0.34	0.39
Cobalt	0.36	0.37
Columbium	0.37	0.40
Copper	0.10	0.15
Erbium	0.55	0.38
Gold	0.14	0.22
Iridium	0.30	...
Iron	0.35	0.37
Manganese	0.59	0.59
Molybdenum	0.37	0.40
Nickel	0.36	0.37
Palladium	0.33	0.37
Platinum	0.30	0.38
Rhodium	0.24	0.30
Silver	0.07	0.07
Tantalum	0.49	...
Thorium	0.36	
Titanium	0.63	
Tungsten	0.43	
Uranium	0.54	0.34
Vanadium	0.35	0.32
Yttrium	0.35	0.35
Zirconium	0.32	0.30
Steel	0.35	0.37
Cast Iron	0.37	0.40
Constantan	0.35	
Monel	0.37	
Chromel P (90Ni-10Cr)	0.35	
80Ni-20Cr	0.35	
60Ni-24Fe-16Cr	0.36	
Alumel (95Ni; Bal. Al, Mn, Si)	0.37	
90Pt-10Rh	0.27	

Table 17. Spectral Emissivity of Oxides.

The emissivity of oxides and oxidized metals depends to a large extent upon the roughness of the surface. In general, higher values of emissivity are obtained on the rougher surfaces.

Material	$\epsilon_{0.65\mu}$ Range of observed values	$\epsilon_{0.65\mu}$ Probable value for the oxide formed on smooth metal
Aluminum oxide	0.22 to 0.40	0.30
Beryllium oxide	0.07 to 0.37	0.35
Cerium oxide	0.58 to 0.80	....
Chromium oxide	0.60 to 0.80	0.70
Cobalt oxide		0.75
Columbium oxide	0.55 to 0.71	0.70
Copper oxide	0.60 to 0.80	0.70
Iron oxide	0.63 to 0.98	0.70
Magnesium oxide	0.10 to 0.43	0.20
Nickel oxide	0.85 to 0.96	0.90
Thorium oxide	0.20 to 0.57	0.50
Tin oxide	0.32 to 0.60	....
Titanium oxide		0.50
Uranium oxide		0.30
Vanadium oxide		0.70
Yttrium oxide		0.60
Zirconium oxide	0.18 to 0.43	0.40
Alumel (oxidized)		0.87
Cast Iron (oxidized)		0.70
Chromel P (90Ni-10Cr) (oxidized)		0.87
80Ni-20Cr (oxidized)		0.90
60Ni-24Fe-16Cr (oxidized)		0.83
55Fe-37.5Cr-7.5Al (oxidized)		0.78
70Fe-23Cr-5Al-2Co (oxidized)		0.75
Constantan (55Cu-45Ni) (oxidized)		0.84
Carbon Steel (oxidized)		0.80
Stainless Steel (18-8) (oxidized)		0.85
Porcelain	0.25 to 0.50	

Table 18. Total Emissivity of Metals, Surface Unoxidized.

Material	ϵ_t					
	25 °C	100 °C	500 °C	1000 °C	1500 °C	2000 °C
Aluminum	0.022	0.028	0.060	......	......	......
Bismuth	0.048	0.061	......	......	......	......
Carbon	0.081	0.081	0.079	......	......	......
Chromium	......	0.08	......	......	......	......
Cobalt	......	......	0.13	0.23	......	......
Columbium	......	......	......	......	0.19	0.24
Copper	......	0.02	......	(Liquid 0.15)	......	......
Gold	......	0.02	0.03	......	......	......
Iron	......	0.05	......	......	......	......
Lead	......	0.05	......	......	......	......
Mercury	0.10	0.12	......	......	......	......
Molybdenum	......	......	......	0.13	0.19	0.24
Nickel	0.045	0.06	0.12	0.19	......	......
Platinum	0.037	0.047	0.096	0.152	0.191	......
Silver	......	0.02	0.035	......	......	......
Tantalum	......	......	......	......	0.21	0.26
Tin	0.043	0.05	......	......	......	......
Tungsten	0.024	0.032	0.071	0.15	0.23	0.28
Zinc	(0.05 at 300 °C)					
Brass	0.035	0.035	......	......	......	......
Cast iron	......	0.21		(Liquid 0.29)		
Steel	......	0.08		(Liquid 0.28)		

Table 19. Total Emissivity of Miscellaneous Materials. (Most values are uncertain by 10% to 30%. In many cases value depends on particle size.)

Material	Temp. (°C)	ϵ_t
Aluminum (oxidized)	200 600	0.11 0.19
Brass (oxidized)	200 600	0.61 0.59
Calorized copper	100 500	0.26 0.26
Calorized copper (oxidized)	200 600	0.18 0.19
Calorized steel (oxidized)	200 600	0.52 0.57
Cast iron (strongly oxidized)	40 250	0.95 0.95
Cast iron (oxidized)	200 600	0.64 0.78
Copper (oxidized)	200 1000	0.6 0.6
Fire brick	1000	0.75
Gold enamel	100	0.37
Iron (oxidized)	100 500 1200	0.74 0.84 0.89
Iron (rusted)	25	0.65
Lead (oxidized)	200	0.63
Monel (oxidized)	200 600	0.43 0.43
Nickel (oxidized)	200 1200	0.37 0.85
Silica brick	1000 1100	0.80 0.85
Steel (oxidized)	25 200 600	0.80 0.79 0.79
Steel plate (rough)	40 400	0.94 0.97
Wrought iron (dull oxidized)	25 350	0.94 0.94
20Ni-25Cr-55Fe (oxidized)	200 500	0.90 0.97
60Ni-12Cr-28Fe (oxidized)	270 560	0.89 0.82
80Ni-20Cr (oxidized)	100 600 1300	0.87 0.87 0.89

Table 20. True Temperatures Corresponding to Various Emissivities and Various Brightness Temperatures Observed with an Optical Pyrometer. The Temperatures, in °C, are for $\lambda = 0.65\ \mu$ and $c_2 = 1.432$ cm deg.

Spectral	Observed temperature in headings, true temperature in the body of the table										
Emissivity	700	800	900	1000	1100	1200	1300	1400	1600	1800	2000
0.05	848	983	1123	1266	1415	1569	1728	1849	2240	2614	3017
0.10	810	935	1064	1195	1330	1468	1609	1754	2056	2373	2708
0.15	789	909	1032	1157	1284	1414	1546	1682	1960	2250	2552
0.20	774	891	1010	1130	1253	1378	1504	1633	1897	2170	2453
0.25	763	878	993	1111	1230	1350	1473	1597	1850	2111	2379
0.30	755	867	980	1095	1211	1329	1448	1568	1814	2065	2322
0.35	747	858	969	1082	1196	1311	1427	1545	1783	2027	2276
0.40	741	850	960	1071	1183	1296	1410	1525	1758	1996	2237
0.45	736	843	952	1062	1172	1283	1395	1508	1736	1968	2204
0.50	731	837	945	1053	1162	1272	1382	1493	1717	1945	2175
0.55	726	832	939	1046	1153	1261	1370	1480	1700	1923	2149
0.60	722	827	933	1039	1145	1252	1360	1467	1685	1905	2126
0.65	719	823	927	1032	1138	1244	1350	1457	1671	1888	2106
0.70	716	819	923	1027	1131	1236	1341	1447	1659	1872	2087
0.75	712	815	917	1021	1125	1229	1333	1437	1647	1858	2069
0.80	710	812	914	1017	1119	1222	1325	1429	1636	1844	2054
0.85	707	809	910	1012	1114	1216	1318	1421	1626	1832	2039
0.90	704	805	907	1008	1109	1210	1312	1413	1617	1821	2025
0.95	702	803	903	1004	1104	1205	1306	1407	1608	1810	2012
1.00	700	800	900	1000	1100	1200	1300	1400	1600	1800	2000

Table 21. True Temperatures C[illegible] and Various Brightness Temperatures.

(All temperatures in °C.)

Total Emissivity	*Observed temperature in headings, true temperature in body of table*										
	100	200	300	400	600	800	1000	1200	1400	1600	1800
0.05	422	686	916	1137	1567	1993	2317	2841	3264	3687	4110
0.10	316	536	728	913	1275	1632	1989	2345	2701	3057	3413
0.15	264	460	633	799	1126	1449	1771	2093	2415	2736	3058
0.20	231	410	571	725	1029	1330	1629	1929	2228	2527	2827
0.25	207	375	526	672	958	1243	1526	1809	2093	2376	2658
0.30	189	347	491	630	904	1175	1446	1717	1987	2258	2528
0.35	175	325	463	596	860	1121	1381	1642	1902	2162	2422
0.40	164	307	439	568	823	1075	1327	1579	1830	2082	2333
0.45	154	291	419	544	791	1036	1281	1525	1769	2014	2258
0.50	146	278	402	523	763	1002	1240	1478	1716	1954	2192
0.55	138	266	387	505	739	972	1204	1437	1669	1902	2134
0.60	132	255	373	489	718	945	1173	1400	1628	1855	2082
0.65	126	246	361	474	698	921	1144	1367	1590	1813	2036
0.70	121	238	350	461	680	900	1119	1337	1556	1775	1993
0.75	117	230	340	448	664	880	1095	1310	1525	1740	1955
0.80	113	223	331	437	649	861	1073	1284	1496	1707	1919
0.85	109	217	322	427	636	844	1053	1261	1469	1678	1886
0.90	106	211	314	417	623	828	1034	1239	1445	1650	1855
0.95	103	205	307	408	611	814	1016	1219	1422	1624	1827
1.00	100	200	300	400	600	800	1000	1200	1400	1600	1800

Table 22. Properties of Tungsten. (The values of ϵ_c, T_c, and $T_{0.65\mu}$ have been calculated from the spectral emissivities $\epsilon_{0.65\mu}$ and $\epsilon_{0.467\mu}$.)

True Temperature (T °K)	Relative Resistance (R_T/R_{293})	Normal Brightness (New Candles per cm²)	Spectral Emissivity $\epsilon_{0.65\mu}$	Spectral Emissivity $\epsilon_{0.467\mu}$	Color Emissivity (ϵ_c)	Total Emissivity ϵ_t	Brightness Temperature $T_{0.65\mu}$	Color Temper ture T_c
300	1.12		0.472	0.505		0.032		
400	1.58					.042		
500	2.07					.053		
600	2.58					.064		
700	3.11					.076		
800	3.65					.088		
900	4.21					.101		
1000	4.78	0.0001	.458	.486	0.395	.114	966	1007
1100	5.36	0.001	.456	.484	.392	.128	1059	1108
1200	5.95	0.006	.454	.482	.390	.143	1151	1210
1300	6.55	0.029	.452	.480	.387	.158	1242	1312
1400	7.16	0.11	.450	.478	.385	.175	1332	1414
1500	7.78	0.33	.448	.476	.382	.192	1422	1516
1600	8.41	0.92	.446	.475	.380	.207	1511	1619
1700	9.04	2.3	.444	.473	.377	.222	1599	1722
1800	9.69	5.1	.442	.472	.374	.236	1687	1825
1900	10.34	10.4	.440	.470	.371	.249	1774	1929
2000	11.00	20.0	.438	.469	.368	.260	1861	2032
2100	11.65	36	.436	.467	.365	.270	1946	2136
2200	12.33	61	.434	.466	.362	.279	2031	2241
2300	13.01	101	.432	.464	.359	.288	2115	2345
2400	13.69	157	.430	.463	.356	.296	2198	2451
2500	14.38	240	.428	.462	.353	.303	2280	2556
2600	15.08	350	.426	.460	.349	.311	2362	2662
2700	15.78	500	.424	.459	.346	.318	2443	2769
2800	16.48	690	.422	.458	.343	.323	2523	2876
2900	17.19	950	.420	.456	.340	.329	2602	2984
3000	17.90	1260	.418	.455	.336	.334	2681	3092
3100	18.62	1650	.416	.454	.333	.337	2759	3200
3200	19.35	2100	.414	.452	.330	.341	2837	3310
3300	20.08	2700	.412	.451	.326	.344	2913	3420
3400	20.82	3400	.410	.450	.323	.348	2989	3530
3500	21.56	4200	.408	.449	.320	.351	3063	3642
3600	22.30	5200	.406	.447	.317	.354	3137	3754

Table 23. Conversion Table: Degrees Centigrade to Degrees Fahrenheit.

°C	0	10	20	30	40	50	60	70	80	90
	F	F	F	F	F	F	F	F	F	F
−200	−328	−346	−364	−382	−400	−418	−436	−454	....	....
−100	−148	−166	−184	−202	−220	−238	−256	−274	−292	−310
−0	+32	+14	−4	−22	−40	−58	−76	−94	−112	−130
0	32	50	68	86	104	122	140	158	176	194
100	212	230	248	266	284	302	320	338	356	374
200	392	410	428	446	464	482	500	518	536	554
300	572	590	608	626	644	662	680	698	716	734
400	752	770	788	806	824	842	860	878	896	914
500	932	950	968	986	1004	1022	1040	1058	1076	1094
600	1112	1130	1148	1166	1184	1202	1220	1238	1256	1274
700	1292	1310	1328	1346	1364	1382	1400	1418	1436	1454
800	1472	1490	1508	1526	1544	1562	1580	1598	1616	1634
900	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814
1000	1832	1850	1868	1886	1904	1922	1940	1958	1976	1994
1100	2012	2030	2048	2066	2084	2102	2120	2138	2156	2174
1200	2192	2210	2228	2246	2264	2282	2300	2318	2336	2354
1300	2372	2390	2408	2426	2444	2462	2480	2498	2516	2534
1400	2552	2570	2588	2606	2624	2642	2660	2678	2696	2714
1500	2732	2750	2768	2786	2804	2822	2840	2858	2876	2894
1600	2912	2930	2948	2966	2984	3002	3020	3038	3056	3074
1700	3092	3110	3128	3146	3164	3182	3200	3218	3236	3254
1800	3272	3290	3308	3326	3344	3362	3380	3398	3416	3434
1900	3452	3470	3488	3506	3524	3542	3560	3578	3596	3614
2000	3632	3650	3668	3686	3704	3722	3740	3758	3776	3794
2100	3812	3830	3848	3866	3884	3902	3920	3938	3956	3974
2200	3992	4010	4028	4046	4064	4082	4100	4118	4136	4154
2300	4172	4190	4208	4226	4244	4262	4280	4298	4316	4334
2400	4352	4370	4388	4406	4424	4442	4460	4478	4496	4514
2500	4532	4550	4568	4586	4604	4622	4640	4658	4676	4694
2600	4712	4730	4748	4766	4784	4802	4820	4838	4856	4874
2700	4892	4910	4928	4946	4964	4982	5000	5018	5036	5054
2800	5072	5090	5108	5126	5144	5162	5180	5198	5216	5234
2900	5252	5270	5288	5306	5324	5342	5360	5378	5396	5414
3000	5432	5450	5468	5486	5504	5522	5540	5558	5576	5594
3100	5612	5630	5648	5666	5684	5702	5720	5738	5756	5774
3200	5792	5810	5828	5846	5864	5882	5900	5918	5936	5954
3300	5972	5990	6008	6026	6044	6062	6080	6098	6116	6134
3400	6152	6170	6188	6206	6224	6242	6260	6278	6296	6314
3500	6332	6350	6368	6386	6404	6422	6440	6458	6476	6494
3600	6512	6530	6548	6566	6584	6602	6620	6638	6656	6674
3700	6692	6710	6728	6746	6764	6782	6800	6818	6836	6854
3800	6872	6890	6908	6926	6944	6962	6980	6998	7016	7034
3900	7052	7070	7088	7106	7124	7142	7160	7178	7196	7214
°C	0	10	20	30	40	50	60	70	80	90

°C	°F
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2
10	18.0

°F	°C
1	0.56
2	1.11
3	1.67
4	2.22
5	2.78
6	3.33
7	3.89
8	4.44
9	5.00
10	5.56
11	6.11
12	6.67
13	7.22
14	7.78
15	8.33
16	8.89
17	9.44
18	10.00

Examples: 1347 °C = 2444 °F + 12.6 °F = 2456.6 °F. 3366 °F = 1850 °C + 2.78 °C = 1852.78 °C.

Table 24. Conversion Table: Degrees Fahrenheit to Degrees Centigrade.
(Single boldface figures indicate recurring decimals.)

°F	0	10	20	30	40	50	60	70	80	90
	C	C	C	C	C	C	C	C	C	C
−400	−240.0	−245.5	−251.1	−256.6	−262.2	−267.7	......	......	......	......
−300	−184.4	−190.0	−195.5	−201.1	−206.6	−212.2	−217.7	−223.3	−228.8	−234.4
−200	−128.8	−134.4	−140.0	−145.5	−151.1	−156.6	−162.2	−167.7	−173.3	−178.8
−100	−73.3	−78.8	−84.4	−90.0	−95.5	−101.1	−106.6	−112.2	−117.7	−123.3
−0	−17.7	−23.3	−28.8	−34.4	−40.0	−45.5	−51.1	−56.6	−62.2	−67.7
0	−17.7	−12.2	−6.6	−1.1	+4.4	+10.0	+15.5	+21.1	+26.6	+32.2
100	37.7	43.3	48.8	54.4	60.0	65.5	71.1	76.6	82.2	87.7
200	93.3	98.8	104.4	110.0	115.5	121.1	126.6	132.2	137.7	143.3
300	148.8	154.4	160.0	165.5	171.1	176.6	182.2	187.7	193.3	198.8
400	204.4	210.0	215.5	221.1	226.6	232.2	237.7	243.3	248.8	254.4
500	260.0	265.5	271.1	276.6	282.2	287.7	293.3	298.8	304.4	310.0
600	315.5	321.1	326.6	332.2	337.7	343.3	348.8	354.4	360.0	365.5
700	371.1	376.6	382.2	387.7	393.3	398.8	404.4	410.0	415.5	421.1
800	426.6	432.2	437.7	443.3	448.8	454.4	460.0	465.5	471.1	476.6
900	482.2	487.7	493.3	498.8	504.4	510.0	515.5	521.1	526.6	532.2
1000	537.7	543.3	548.8	554.4	560.0	565.5	571.1	576.6	582.2	587.7
1100	593.3	598.8	604.4	610.0	615.5	621.1	626.6	632.2	637.7	643.3
1200	648.8	654.4	660.0	665.5	671.1	676.6	682.2	687.7	693.3	698.8
1300	704.4	710.0	715.5	721.1	726.6	732.2	737.7	743.3	748.8	754.4
1400	760.0	765.5	771.1	776.6	782.2	787.7	793.3	798.8	804.4	810.0
1500	815.5	821.1	826.6	832.2	837.7	843.3	848.8	854.4	860.0	865.5
1600	871.1	876.6	882.2	887.7	893.3	898.8	904.4	910.0	915.5	921.1
1700	926.6	932.2	937.7	943.3	948.8	954.4	960.0	965.5	971.1	976.6
1800	982.2	987.7	993.3	998.8	1004.4	1010.0	1015.5	1021.1	1026.6	1032.2
1900	1037.7	1043.3	1048.8	1054.4	1060.0	1065.5	1071.1	1076.6	1082.2	1087.7
2000	1093.3	1098.8	1104.4	1110.0	1115.5	1121.1	1126.6	1132.2	1137.7	1143.3
2100	1148.8	1154.4	1160.0	1165.5	1171.1	1176.6	1182.2	1187.7	1193.3	1198.8
2200	1204.4	1210.0	1215.5	1221.1	1226.6	1232.2	1237.7	1243.3	1248.8	1254.4
2300	1260.0	1265.5	1271.1	1276.6	1282.2	1287.7	1293.3	1298.8	1304.4	1310.0
2400	1315.5	1321.1	1326.6	1332.2	1337.7	1343.3	1348.8	1354.4	1360.0	1365.5
2500	1371.1	1376.6	1382.2	1387.7	1393.3	1398.8	1404.4	1410.0	1415.5	1421.1
2600	1426.6	1432.2	1437.7	1443.3	1448.8	1454.4	1460.0	1465.5	1471.1	1476.6
2700	1482.2	1487.7	1493.3	1498.8	1504.4	1510.0	1515.5	1521.1	1526.6	1532.2
2800	1537.7	1543.3	1548.8	1554.4	1560.0	1565.5	1571.1	1576.6	1582.2	1587.7
2900	1593.3	1598.8	1604.4	1610.0	1615.5	1621.1	1626.6	1632.2	1637.7	1643.3
3000	1648.8	1654.4	1660.0	1665.5	1671.1	1676.6	1682.2	1687.7	1693.3	1698.8
3100	1704.4	1710.0	1715.5	1721.1	1726.6	1732.2	1737.7	1743.3	1748.8	1754.4
3200	1760.0	1765.5	1771.1	1776.6	1782.2	1787.7	1793.3	1798.8	1804.4	1810.0
3300	1815.5	1821.1	1826.6	1832.2	1837.7	1843.3	1848.8	1854.4	1860.0	1865.5
3400	1871.1	1876.6	1882.2	1887.7	1893.3	1898.8	1904.4	1910.0	1915.5	1921.1
3500	1926.6	1932.2	1937.7	1943.3	1948.8	1954.4	1960.0	1965.5	1971.1	1976.6
3600	1982.2	1987.7	1993.3	1998.8	2004.4	2010.0	2015.5	2021.1	2026.6	2032.2
°F	0	10	20	30	40	50	60	70	80	90

	°C
	0.5
	1.1
	1.6
4	2.2
5	2.7
6	3.3
7	3.8
8	4.4
9	5.0

Examples: −246.0 °F = −151.11 °C − 3.33 °C = −154.44 °C.
3762 °F = 2071.1 °C + 1.1 °C = 2072.2 °C.
2423.5 °F = 1326.66 °C + 1.66 °C + 0.27 °C = 1328.61 °C.

Table 24.—(*Continued*).

°F to °C.

°F	0	10	20	30	40	50	60	70	80	90
	C	C	C	C	C	C	C	C	C	C
3700	2037.7	2043.3	2048.8	2054.4	2060.0	2065.5	2071.1	2076.6	2082.2	2087.7
3800	2093.3	2098.8	2104.4	2110.0	2115.5	2121.1	2126.6	2132.2	2137.7	2143.3
3900	2148.8	2154.4	2160.0	2165.5	2171.1	2176.6	2182.2	2187.7	2193.3	2198.8
4000	2204.4	2210.0	2215.5	2221.1	2226.6	2232.2	2237.7	2243.3	2248.8	2254.4
4100	2260.0	2265.5	2271.1	2276.6	2282.2	2287.7	2293.3	2298.8	2304.4	2310.0
4200	2315.5	2321.1	2326.6	2332.2	2337.7	2343.3	2348.8	2354.4	2360.0	2365.5
4300	2371.1	2376.6	2382.2	2387.7	2393.3	2398.8	2404.4	2410.0	2415.5	2421.1
4400	2426.6	2432.2	2437.7	2443.3	2448.8	2454.4	2460.0	2465.5	2471.1	2476.6
4500	2482.2	2487.7	2493.3	2498.8	2504.4	2510.0	2515.5	2521.1	2526.6	2532.2
4600	2537.7	2543.3	2548.8	2554.4	2560.0	2565.5	2571.1	2576.6	2582.2	2587.7
4700	2593.3	2598.8	2604.4	2610.0	2615.5	2621.1	2626.6	2632.2	2637.7	2643.3
4800	2648.8	2654.4	2660.0	2665.5	2671.1	2676.6	2682.2	2687.7	2693.3	2698.8
4900	2704.4	2710.0	2715.5	2721.1	2726.6	2732.2	2737.7	2743.3	2748.8	2754.4
5000	2760.0	2765.5	2771.1	2776.6	2782.2	2787.7	2793.3	2798.8	2804.4	2810.0
5100	2815.5	2821.1	2826.6	2832.2	2837.7	2843.3	2848.8	2854.4	2860.0	2865.5
5200	2871.1	2876.6	2882.2	2887.7	2893.3	2898.8	2904.4	2910.0	2915.5	2921.1
5300	2926.6	2932.2	2937.7	2943.3	2948.8	2954.4	2960.0	2965.5	2971.1	2976.6
5400	2982.2	2987.7	2993.3	2998.8	3004.4	3010.0	3015.5	3021.1	3026.6	3032.2
5500	3037.7	3043.3	3048.8	3054.4	3060.0	3065.5	3071.1	3076.6	3082.2	3087.7
5600	3093.3	3098.8	3104.4	3110.0	3115.5	3121.1	3126.6	3132.2	3137.7	3143.3
5700	3148.8	3154.4	3160.0	3165.5	3171.1	3176.6	3182.2	3187.7	3193.3	3198.8
5800	3204.4	3210.0	3215.5	3221.1	3226.6	3232.2	3237.7	3243.3	3248.8	3254.4
5900	3260.0	3265.5	3271.1	3276.6	3282.2	3287.7	3293.3	3298.8	3304.4	3310.0
6000	3315.5	3321.1	3326.6	3332.2	3337.7	3343.3	3348.8	3354.4	3360.0	3365.5
6100	3371.1	3376.6	3382.2	3387.7	3393.3	3398.8	3404.4	3410.0	3415.5	3421.1
6200	3426.6	3432.2	3437.7	3443.3	3448.8	3454.4	3460.0	3465.5	3471.1	3476.6
6300	3482.2	3487.7	3493.3	3498.8	3504.4	3510.0	3515.5	3521.1	3526.6	3532.2
6400	3537.7	3543.3	3548.8	3554.4	3560.0	3565.5	3571.1	3576.6	3582.2	3587.7
6500	3593.3	3598.8	3604.4	3610.0	3615.5	3621.1	3626.6	3632.2	3637.7	3643.3
6600	3648.8	3654.4	3660.0	3665.5	3671.1	3676.6	3682.2	3687.7	3693.3	3698.8
6700	3704.4	3710.0	3715.5	3721.1	3726.6	3732.2	3737.7	3743.3	3748.8	3754.4
6800	3760.0	3765.5	3771.1	3776.6	3782.2	3787.7	3793.3	3798.8	3804.4	3810.0
6900	3815.5	3821.1	3826.6	3832.2	3837.7	3843.3	3848.8	3854.4	3860.0	3865.5
7000	3871.1	3876.6	3882.2	3887.7	3893.3	3898.8	3904.4	3910.0	3915.5	3921.1
7100	3926.6	3932.2	3937.7	3943.3	3948.8	3954.4	3960.0	3965.5	3971.1	3976.6
7200	3982.2	3987.7	3993.3	3998.8	4004.4	4010.0	4015.5	4021.1	4026.6	4032.2
7300	4037.7	4043.3	4048.8	4054.4	4060.0	4065.5	4071.1	4076.6	4082.2	4087.7
7400	4093.3	4098.8	4104.4	4110.0	4115.5	4121.1	4126.6	4132.2	4137.7	4143.3
7500	4148.8	4154.4	4160.0	4165.5	4171.1	4176.6	4182.2	4187.7	4193.3	4198.8
7600	4204.4	4210.0	4215.5	4221.1	4226.6	4232.2	4237.7	4243.3	4248.8	4254.4
7700	4260.0	4265.5	4271.1	4276.6	4282.2	4287.7	4293.3	4298.8	4304.4	4310.0
7800	4315.5	4321.1	4326.6	4332.2	4337.7	4343.3	4348.8	4354.4	4360.0	4365.5
7900	4371.1	4376.6	4382.2	4387.7	4393.3	4398.8	4404.4	4410.0	4415.5	4421.1
°F	0	10	20	30	40	50	60	70	80	90

°F	°C
1	0.5
2	1.1
3	1.6
4	2.2
5	2.7
6	3.3
7	3.8
8	4.4
9	5.0

Table 25. The Chemical Elements: their Atomic Numbers, Symbols, and Weights, and their Melting Points on the International Temperature Scale.

Temperatures below −190 °C are on the Centigrade Thermodynamic Scale. The atomic weights given constitute the complete list of the International Weights of 1940, as approved and reported by the Committee on Atomic Weights of the International Union of Chemistry. There is reason to believe that the following (unofficial) values may prove more nearly correct: Aluminum, 26.974; gallium, 69.74.

Atomic No.	Atomic symbol	Name of element	Melting point	Atomic weight	Atomic No.	Atomic symbol	Name of element	Melting point	Atomic weight
			°C					°C	
89	Ac	Actinium	[1]1600		31	Ga	Gallium	29.78 ± 0.02	69.72
13	Al	Aluminum	660.0 ± 0.1	26.97	32	Ge	Germanium	958 ± 10	72.60
51	Sb	Antimony	630.5 ± 0.1	121.76	79	Au	Gold	1063.0 ± 0.0	197.2
18	A	Argon	−189.3 ± 0.5	39.944	72	Hf	Hafnium	[1]1700	178.6
33	As	Arsenic	[2]814	74.91	2	He	Helium	[3]−271.4 ± 0.2	4.003
56	Ba	Barium	704 ± 20	137.36	67	Ho	Holmium		163.5
4	Be	Beryllium	1280 ± 40	9.02	1	H	Hydrogen	−259.2 ± 0.1	1.0080
83	Bi	Bismuth	271.3 ± 0.1	209.00			H_2 (normal)	−259.2 ± 0.1	
5	B	Boron	2300 ± 300	10.82			HD	−256.5 ± 0.2	
35	Br	Bromine	−7.2 ± 0.2	79.916			D_2 (normal)	−254.5 ± 0.2	
48	Cd	Cadmium	320.9 ± 0.1	112.41	61	Il	Illinium		
20	Ca	Calcium	850 ± 20.	40.08	49	In	Indium	156.4 ± 0.1	114.76
6	C	Carbon	3700 ± 100	12.010	53	I	Iodine	114 ± 1	126.92
58	Ce	Cerium	600 ± 50	140.13	77	Ir	Iridium	2454 ± 3	193.1
55	Cs	Cesium	28 ± 2	132.91	26	Fe	Iron	1539 ± 1	55.85
17	Cl	Chlorine	−101 ± 2	35.457	36	Kr	Krypton	−157 ± 0.5	83.7
24	Cr	Chromium	1800 ± 50	52.01	57	La	Lanthanum	826 ± 5	138.92
27	Co	Cobalt	1490 ± 20	58.94	82	Pb	Lead	327.4 ± 0.1	207.21
41	Cb	Columbium	2500 ± 50	92.91	3	Li	Lithium	186 ± 5	6.940
29	Cu	Copper	1083.0 ± 0.1	63.57	71	Lu	Lutecium		174.99
66	Dy	Dysprosium		162.46	12	Mg	Magnesium	650 ± 2	24.32
68	Er	Erbium		167.2	25	Mn	Manganese	1260 ± 20	54.93
63	Eu	Europium		152.0	43	Ma	Masurium	[1]2700	
9	F	Fluorine	−223 ± 10	19.00	80	Hg	Mercury	−38.87 ± 0.02	200.61
64	Gd	Gadolinium		156.9	42	Mo	Molybdenum	2625 ± 50	95.95

[1] Computed. [2] At 36 atmospheres. [3] At 30 atmospheres.

60	Nd	Neodymium......	840	± 40	144.27	47	Ag	Silver...........	960.5	± 0.0	107.880
10	Ne	Neon...........	-248.6	± 0.3	20.183	11	Na	Sodium..........	97.7	± 0.2	22.997
28	Ni	Nickel..........	1455	± 1	58.69	38	Sr	Strontium........	770	± 10	87.63
7	N	Nitrogen........	-210.0	± 0.3	14.008	16	S	Sulfur:			32.06
76	Os	Osmium..........	2700	± 200	190.2			Monoclinic.....	119.2	± 0.2	....
8	O	Oxygen..........	-218.8	± 0.3	16.0000			Rhombic.......	112.8	± 0.2	....
46	Pd	Palladium........	1554	± 1	106.7	73	Ta	Tantalum........	3000	± 100	180.88
15	P	Phosphorus, Y....	44.1	± 0.1	30.98	52	Te	Tellurium........	450	± 10	127.61
		Phosphorus, R....	[1]590			65	Tb	Terbium.........	327	± 5	159.2
78	Pt	Platinum.........	1773.5	± 1	195.23	81	Tl	Thallium.........	300	± 3	204.39
84	Po	Polonium.........	[1]600		....	90	Th	Thorium.........	1800	± 150	232.12
19	K	Potassium........	63	± 1	39.096	69	Tm	Thulium.........	....		169.4
59	Pr	Praseodymium....	940	± 50	140.92	50	Sn	Tin.............	231.9	± 0.1	118.70
91	Pa	Protactinium.....	[1]3000		231	22	Ti	Titanium........	1820	± 100	47.90
88	Ra	Radium..........	700		226.05	74	W	Tungsten........	3410	± 20	183.92
86	Rn	Radon...........	-71		222	92	U	Uranium.........	[1]3600		238.07
75	Re	Rhenium.........	[1]3000		186.31	23	V	Vanadium........	1735	± 50	50.95
45	Rh	Rhodium.........	1966	± 3	102.91	54	Xe	Xenon...........	-112	± 1	131.3
37	Rb	Rubidium........	39	± 1	85.48	70	Yb	Ytterbium.......	....		173.04
44	Ru	Ruthenium.......	2500	± 100	101.7	39	Y	Yttrium..........	1490	± 200	88.92
62	Sm	Samarium........	>1300		150.43	30	Zn	Zinc.............	419.5	± 0.1	65.38
21	Sc	Scandium........	1200		45.10	40	Zr	Zirconium........	1750	± 700	91.22
34	Se	Selenium........	220	± 5	78.96	85	......	Element 85......	[1]250		....
14	Si	Silicon..........	1430	± 20	28.06	87	......	Element 87......	[1]23		....

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[1] At 43 atmospheres.

Glossary

Glossary of Technical Terms

This material was assembled from various authorities (see sources at the end) and was distributed in its original form to the contributors to the Symposium for the purpose of aiding in the coördination of the terminology with respect to temperature in different fields of science and technology. The authors were not asked, however, to alter their manuscripts to make their usage consistent with these definitions. The definitions are included in this volume after the incorporation of a few corrections and changes suggested by authors, for the information of students as well as specialists. The definitions are believed to be correctly descriptive of modern usage but are not to be regarded as standard.

Accuracy. The word *accuracy* has various connotations depending upon the circumstances under which it is used. As applied to a measuring device it is frequently used as a synonym for scale error (see **Scale error**). It is also used to denote the reliability of the indications of an instrument after all known corrections have been applied. As applied to the final result of a measurement, it is used to indicate the estimated maximum amount by which the result may differ from the true value, as differentiated from the reproducibility or "precision" of the measurements (see **Precision**).

Alumel. An alloy of 95 per cent nickel and about 5 per cent aluminum, manganese and silicon, used for thermocouples. A proprietary name.

Automatic reset. An auxiliary functional means in an automatic controller which serves to correct for a permanent change in load or potential of available energy. It is used in controllers of the throttling type, which exhibit a load error without it.

Blackbody. A radiator which, at any specified temperature, emits in each part of the spectrum the maximum energy obtainable per unit time from any radiator as a result of temperature alone.

Bolometer. (1) An instrument in which the resistance of an electrical conductor serves as a measure of the radiant energy incident upon it. (2) An electrical network containing two nearly identical thin strip resistors, one or both of which in use are exposed to radiant energy whose rate of incidence is determined by changes of resistance of one or both of the resistors.

Brightness temperature. Of a body, the temperature of a blackbody having the same brightness at some specified wave-length.

Bulb. The expanded part of the containing system of a fluid-expansion thermometer, which in use is at the place where temperature is to be measured.

Chromel P. An alloy of 90 per cent nickel and the balance principally chromium, used for thermocouples. A proprietary name.

Cold junction. See **Reference junction.**

Color temperature. Of a body, the temperature of a blackbody having the same color.

Constantan. An alloy of 60 to 45 per cent copper and 40 to 55 per cent nickel (with or without small percentages of manganese, iron and carbon). The constantan used for thermocouples contains approximately 55 per cent copper and 45 per cent nickel. No longer a proprietary name.

Controller, direct-acting. An automatic temperature controller arranged to control the rate of supply of heat, as distinguished from one arranged to control the rate of supply of a cooling medium.

Controller, on-off. Also called two-position, or open and shut. An automatic temperature controller capable of selecting one of only two potential levels of heat or cooling supply, one of which may be zero, and dependent upon whether the measured temperature is above or below the control point.

Controller, self-acting. An automatic controller in which the power used to actuate it is taken directly from the medium being controlled, as distinguished from relay-operated controllers.

Controller, three-position. An automatic temperature controller capable of selecting one of only three potential levels of heat supply, and dependent upon whether the measured temperature is above a higher selected temperature, below a lower selected temperature, or between the two values.

Controller, throttling or corresponding. Loosely called proportional. An automatic temperature controller arranged to vary the heat supply as a function of (in correspondence with) the measured temperature independently of variations of any other associated conditions.

Critical damping. Of a galvanometer, the degree of damping required to just prevent oscillation. *Cf.* aperiodic, deadbeat.

d'Arsonval galvanometer. A direct current galvanometer in which the measured current is conducted through a coil of wire supported to rotate between the poles of a permanent magnet against the torsion of a spring or suspension wire. Differentiated from the Thomson or moving magnet galvanometer.

Dead-zone. In a temperature instrument, the interval within which variations of the measured and/or controlled temperature cannot be detected nor result in a controlling action.

Double bridge. A modification of the Wheatstone bridge especially suited to the comparison of conductors having low resistance. The modification consists essentially of replacing the branch point between the two conductors of lowest resistance with a three-element, three-branch point network. Frequently called the Thomson or Kelvin bridge.

Emissivity. The ratio of the radient energy emitted per unit time and per unit area by a body to that emitted by a blackbody at the same temperature. Total emissivity if referring to radiation of all wave-lengths, and monochromatic emissivity if referring to the radiation in a particular wave-length interval. See Index for references to related terms.

Extension leads. A pair of lead wires of such materials that when it is connected to a thermocouple the effective reference junctions will be removed to the other end of the leads.

Follow-up. A term used in the art of automatic temperature control to designate the link means between the measuring and controlling parts of a throttling controller.

Galvanometer. A current-measuring instrument dependent for its action on the magnetic effect of the current being measured.

Gas thermometer. A thermometer in which either the pressure at constant volume of an enclosed gas, or the volume of a gas held at constant pressure serves as a measure of temperature.

Heat. Energy in the process of transfer from one body to another by a thermal process, *i.e.*, by radiation, conduction, or convection.

Homeothermic, homeothermal (Gr. *homoios*, like+*thermos*, hot) *Biol.*, (1) Having an internal apparatus for the automatic regulation of temperature. (2) Maintaining a constant temperature, as warm-blooded animals.

Hot junction. See **Measuring junction.**

Lag, thermometric. The delay in the response of a thermometer to changes of temperature.

Liquid-filled thermometer. A thermometer of which the indications depend upon the expansion of a liquid completely filling an enclosure.

Load error or droop. In the performance of an automatic temperature controller of the throttling type, the change in degrees from the set temperature which accompanies a permanent change in load or in the potential of available energy.

Manganin. An alloy principally of copper, manganese and nickel used for resistors because of its very small temperature coefficient of resistance at room temperatures and its very small thermal emf against copper in this range.

Measuring junction. Sometimes called hot junction. That end of a thermocouple which is subjected to the temperature to be measured.

Optical pyrometer. A pyrometer of which the indications depend upon the brightness at some one wave-length, of the hot body whose temperature is being measured.

Peltier effect. The Peltier effect is the absorption or evolution of heat at the junction of two dissimilar metals during the passage of an electric current. The corresponding emf at the junction is called the Peltier emf.

Poikilothermic, poikilothermal (Gr. *poikilos,* changeful + *thermos,* hot) *Biol.,* (1) Having no internal apparatus for the automatic regulation of temperature. (2) Varying in bodily temperature with the surrounding medium. as cold-blooded animals.

Potentiometer. An electrical network used for the measurement of voltages, in which the fall of potential over a known part of a conductor is balanced against the voltage to be measured. Sometimes used unfortunately in the radio art to designate a voltage divider.

Precision. The closeness of agreement of repeated measurements of the same quantity. It is customarily limited to one instrument or to the results obtained with one instrument under one set of conditions.

Pyrometer. A device for measuring high temperatures. *Cf.* **thermometer.**

Radiation Pyrometer. A pyrometer of which the indications depend upon the radiancy of a source of radiant energy. See Index for references to related terms.

Radiation temperature. Of a body, the temperature of a blackbody emitting the same total amount of radiant energy per unit time and per unit area.

Range. Of a temperature-measuring instrument, the span in degrees of its calibrated scale.

Reference junction. Sometimes called cold junction. That end of a thermocouple which is either subjected to a known temperature or is so located with respect to suitable measuring equipment that changes in its temperature are without effect upon the measurement of the temperature of the measuring junction. Usually there are two or more reference junctions in a thermoelectric circuit, so arranged that all of them are maintained at one temperature.

Relay. A device used to transmit impulses from one system to another.

Resistance thermometer. A thermometer in which the electrical resistance of a definite part, the resistor, serves as a measure of temperature.

Scale correction. The amount that must be added algebraically to the scale reading of a measuring instrument to obtain the correct reading.

Scale error. Of a measuring instrument, the algebraic difference between the reading of its scale and the magnitude of the quantity giving rise to that reading. It is equal, but opposite in sign, to the scale correction.

Seebeck effect. The generation of a current in a circuit of two dissimilar metals the junctions of which are at different temperatures.

Sensitivity. Sometimes called unit sensitivity. (1) The response of a measuring instrument to unit change in the quantity being measured. (2) In an automatic temperature controller of the throttling or corresponding type, the inverse ratio of a measured departure from the set temperature to the resulting change in heat input expressed as an equivalent change in temperature. (3) Sometimes used to describe the extent of the "dead-zone."

Temperature. The temperature of a body is its thermal state considered with reference to its ability to communicate heat to other bodies.

Temperature coefficient. The temperature coefficient of a property, u, is the partial derivative of u with respect to temperature, divided by u.

Thermal analysis, thermoanalysis. The investigation of physical transition processes or of chemical reactions by observing discontinuities in the absorption or evolution of heat, manifested by abrupt changes in temperature.

Thermocouple. A pair of dissimilar electrically conducting materials joined together at one end, in which a difference in temperature of the junction from that of the other ends generates an emf.

Thermoelectric pyrometer. A thermoelectric thermometer used for measuring high temperature.

Thermoelectric thermometer. A thermometer, the indications of which depend upon the emf of a thermocouple. It ordinarily consists of a thermocouple, an instrument for measuring emf, and connecting leads.

Thermometer. A device for measuring temperatures.

Thermopile. A battery of thermocouples joined in series to form a single compact unit.

Thermostat. A device for the automatic control or regulation of temperature. The term is generally used to distinguish such a device having no temperature-indicating scale, from an automatic indicating controller.

Thermotaxic. *Physiol.* Pertaining to, or connected with, the regulation of temperature in the body.

Thomson effect. The reversible absorption or evolution of heat in that part of a homogeneous conductor in which there is a temperature gradient, due to the passage of an electric current. The corresponding emf in the temperature gradient of a homogeneous conductor is called the Thomson emf.

Vapor-pressure thermometer. A thermometer of which the indications depend upon the vapor-pressure of a liquid partially filling an enclosure.

Wheatstone bridge. An electrical network consisting of four resistance elements and four branch points, of which one pair of alternate branch points are connected by a source of emf and the other pair of branch points are connected by a detector. A simple relation exists between the resistance elements when the detector connects points of equal potential.

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Indexes

The author and subject indexes were compiled by G. G. Hawley, of the Reinhold Publishing Corporation staff, from suggested entries submitted by the authors. In an attempt to solve the troublesome problem of terminology, the *wording* of the entries has usually been arranged to agree with that of the text at the point of reference, even though this practice necessitates such duplications as *Thermal gradient of earth* and *Geothermal gradient.* In these and other cases, cross references have been liberally supplied. An effort has been made to cover the material on a given topic as thoroughly as possible by means of sub-entries; but this effort is by no means infallible. The indulgence of the reader is therefore requested for such lapses as occur in this respect.

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The names of authors of papers in this volume appear in bold face type.

Superscripts to page numbers indicate the bibliography reference number to the author's work cited on that page. In such cases the author's name does not appear on the page referred to.

A question mark following a name indicates that, in the absence of initials, there is doubt as to the author's identity with others of the same name.

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